

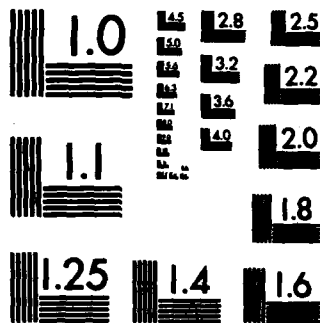
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CALCULATION OF FRANCK-CONDON FACTORS  
FOR DIATOMIC MOLECULES

THESIS

LeAnn D. Brasure  
First Lieutenant, USAF

AFIT/GNE/PH/85M-1

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CALCULATION OF FRANCK-CONDON FACTORS  
FOR DIATOMIC MOLECULES

THESIS

Presented to the Faculty of the School of Engineering  
of the Air Force Institute of Technology

Air University

In Partial Fulfillment of the  
Requirements for the Degree of  
Master of Science in Nuclear Physics

LeAnn D. Brasure, B.S.

First Lieutenant, USAF

March 1985

Approved for public release; distribution unlimited

## Preface

The purpose of this work was to gather data and calculate Franck-Condon Factors for several of the diatomic halogen and interhalogen molecules. Currently there is a renewed interest in these values with the hope that they may both aid the spectroscopist in understanding experimental observations and aid research into new lasing systems by providing early knowledge of the probabilities of transitions occurring between excited states of these molecules.

I enjoyed working on this project and I feel that I have learned a great deal through doing it. I would especially like to thank my advisor, Dr. Ernest A. Dorko, for taking the time to explain all of the required background material to me. Doing a topic outside of my class area meant that I had many new and strange ideas to learn. With Dr. Dorko's help, I gained a great deal of understanding in a subject new to me.

One of the most challenging and frustrating aspects of this thesis was learning the computer operating system and running the programs. I would like to thank Major Tom Hopkins for his good-natured help and for answering all of my many computer questions. Finally, I would like to thank my husband and fellow classmate, for going through it all with me.

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### Abstract

This study calculated Franck-Condon Factors for several diatomic molecules. For one of the molecules, lead oxide, the molecular constants required to do the calculations were obtained from experimental observations of the compound performed at AFIT. Potential energy curves were generated for eight excited states (a, b, A, B, C, C', D, E) and the ground state (X). Franck-Condon Factors were calculated for the transitions of each excited state to the ground state as well as the A to a and D to a transitions. Data obtained from the open literature was used for the remaining five halogens or interhalogens studied; molecular bromine, bromine chloride, bromine monofluoride, iodine chloride, iodine monofluoride. The electronic states modelled and the transitions between states for which Franck-Condon Factors were calculated varied with each molecule.

The potential energy curves were modelled using a program written by Dr. C. R. Vidal of the Max-Planck Institute in Garmisch, Germany. The program uses a Rydberg-Klein-Rees approximation to initially model the curves. These values are then shifted and refined using an Inverted Perturbation Approach routine. This is an iterative procedure which increases the accuracy of the final potential, especially in the higher energy regions. The RKR-IPA program also solves the Schrodinger Wave Equation for each vibrational level and creates a file containing a list

of wavefunction values for each level at a specified number of points along the interval of internuclear separation of interest. The Franck-Condon Factors are calculated using a program written by Capt Joseph Pow and modified in this work to upgrade the approximation of the overlap integral from a simple histogram approach to a Simpson's Rule approximation. The Franck-Condon Factors calculated in this work were then compared to values found in the literature. Good agreement between the most probable transitions (the Condon Parabola) of each set of factors was found even though the numerical values of the two sets differed. This shows that the less accurate RKR approach is sufficient for many uses of Franck-Condon Factors.

# CALCULATION OF FRANCK-CONDON FACTORS FOR DIATOMIC MOLECULES

## I. INTRODUCTION:

Many properties of a diatomic molecule can be described by a set of potential well functions, one for each electronic state of the molecule. Transitions between two states can be described by looking at a spectrum or the properties of the transition can be modelled by considering the potentials of the two states. When the wavefunctions for vibrational levels within the electronic states are combined through the Franck-Condon Factor the probability of that transition occurring can be predicted. This is especially useful to those developing new lasing systems which depend heavily upon optimizing transitions from select molecular energy states. Prior knowledge of the probabilities of such transitions can allow more knowledgable selection of the materials to be tested.

The calculation of these Franck-Condon Factors makes use of molecular constants which are determined from experimental observations made by spectroscopists. These constants are used in the calculation of the potential well for the electronic state. This potential is then used to solve the Schroedinger equation to give the energy and the wavefunction for each vibrational energy level. The two wavefunctions

(one from each state) are multiplied together and integrated over the region where they overlap. The square of this integral is the Franck-Condon Factor. Spectroscopists also use the factors to confirm or deny their transition assignments to lines in an observed spectrum.

This thesis effort will concentrate on the calculation of Franck-Condon Factors for diatomic molecules. In particular, PbO will be investigated using molecular constants determined in a recent thesis effort (11). PbO was previously investigated in a thesis by Capt Joseph J. Pow (20). Results of the two calculations are compared for one of the states of lead oxide. In addition, Franck-Condon Factors will be generated for interhalogens of interest; ICl, IF, Br (molecular), BrCl, and BrF. The potentials and wavefunctions were generated by a program originally written by Dr. C.R. Vidal of the Max-Planck Institut fur Physik und Astrophysik in Garmisch, Germany. This program makes use of the Rydberg-Klein-Rees (RKR) method to approximate the potential. The program also includes an Inverse Perturbational Analysis (IPA) to "fit" the potential curve better at the higher energy values (10: 22 Aug). The IPA routine is optional and may be bypassed if desired. Vidal's program was written to run on a Cray computer and therefore had to be adapted to run on the CDC Cyber computer available to AFIT through the Aeronautical Systems Division. This was done by Capt Lyle L. Rutger in his 1983 thesis (22). Using the output from Rutger's efforts, Pow wrote a program to

correctly allign the wavefunctions and generate Franck-Condon Factors. The integration routine was upgraded to a Simpson's Rule approximation from a histogram approach for the present thesis.

## II. LITERATURE AND BACKGROUND THEORY:

The generation of the vibrational wavefunctions is central to calculation of Franck-Condon Factors. In order to do this a numerical solution to the Schrodinger Wave Equation must first be found. This in turn requires knowledge about the form of the potential,  $U(x)$ . The potential model used for these calculations is a Rydberg-Klein-Rees (RKR) approximation with an Inverted Perturbation Analysis (IPA) used to increase the accuracy of the model at higher energy states. The RKR approach is used when the molecular constants for each energy state are known and the form of the potential is desired. Values for the constants can be obtained from any source and are expressed in units of inverse centimeters. The values reported in this work were obtained from the open literature, past theses, or recent spectroscopic observation performed here at AFIT. These values satisfy the Dunham Equation (Equation 1), which is a power series used to model the energy of a vibrating rotator which serves as a model for the diatomic molecule.

$$T = \sum_{lj} Y_{lj} (v+1/2)^l J^j (J+1)^j \quad (1)$$

Here,  $T$  is the total energy, the  $Y_{lj}$  's are known as the Dunham coefficients,  $v$  is the vibrational quantum number, and  $J$  is the rotational quantum number (15:109). When the expanded power series is truncated so that  $j$  equals only 0 or 1, the  $Y_{lj}$  's become the molecular constants  $\omega_e$ ,  $\omega_e x_e$ ,  $B_e$ ,  $\alpha$ ,

$D_e$ , etc. used in the calculation of the potential.

Briefly, the steps which lead to the calculation of the wavefunctions are as follows. First, a pair of classical turning points is generated for each vibrational level. These points define the classical boundary of the potential well and also "pin down" the shape of the well for future operations such as plotting the potentials. Next, with  $U(x)$  approximated by the turning points, the Wave Equation is solved at each vibrational level with  $J=0$ . This yields the vibrational wavefunction which is used in connection with another vibrational wavefunction to calculate the Franck-Condon Factor.

The calculation of the potential well begins with equation 1 which is rewritten with the vibrational and rotational energies split into separate terms,  $G_v$  and  $B_v J(J+1)$  respectively. Both terms are written for a vibrational level, and  $T$  is equal to the energy (vibrational + rotational) for that  $v$  level. The rewritten equation is shown here as equation 2.

$$T = E_v + E_r = G_v + B_v J(J+1) \quad (2)$$

$G_v$  becomes the purely vibrational terms ( $j=0$ ) and can be written as a power series in  $(v + 1/2)$  (10:25 July).

$$\begin{aligned} G_v &= \sum_1 Y_{10} (v+1/2)^1 \\ &= \omega_e (v+1/2) - \omega_e x_e (v+1/2)^2 + \dots \end{aligned} \quad (3)$$

$B_v J(J+1)$  represents the truncated rotational series (here

$j=1$ ) and the applicable cross terms (20:9).

$$\begin{aligned} B_v J(J+1) &= Y_{11} (v+1/2)^1 J(J+1) \\ &= B_0 J(J+1) + \alpha_0 (v+1/2) J(J+1) + \dots \end{aligned} \quad (4)$$

Equations 3 and 4 represent the total vibrational and rotational energy of a diatomic molecule. According to Rees, the number of molecular constants required to equal the accuracy of much spectroscopic data is six (3 vibrational, 2 rotational, 1 cross term). Occasionally the data can be fit to a quadratic and only five are required (one vibrational is dropped) (21:99). The classical turning points occur when the total energy,  $T$ , equals the potential  $U$ . The minimum and maximum internuclear separation (turning points) can be defined in terms of two functions  $f$  and  $g$  (22:30). These two functions can in turn be written as functions of the vibrational and rotational quantum numbers,  $v$  and  $J$ , shown in equations 5a and 5b.

$$f(v, J(J+1)) = \frac{\hbar}{(2\mu)^{1/2}} \int_0^{v'+1/2} \frac{d(v+1/2)}{[U-T(v+1/2, J(J+1))]^{1/2}} \quad (5a)$$

$$g(v, J(J+1)) = \frac{(2\mu)^{1/2}}{\hbar} \int_0^{v'+1/2} \frac{\left. \frac{\partial T}{\partial J(J+1)} \right|_{v+1/2} d(v+1/2)}{[U-T(v+1/2, J(J+1))]^{1/2}} \quad (5b)$$

where  $\mu$  is the reduced mass of the molecule.  $v'$  in the upper integration limit is chosen so that  $U = T(v'+1/2, J(J+1))$  for a fixed value of  $J(J+1)$ .

If  $J=0$  the rotationless energy states will be evaluated leaving only the vibrational term,  $G_v$ , in the energy

equation. This simplification will be applied to the calculation of Franck-Condon Factors covered later in this section. In the calculation of a Franck-Condon Factor the rotational motion of the molecule is ignored and only the vibrational wavefunction is used. The vibrational wavefunction is calculated from a  $J=0$  energy state.

With  $J=0$  equation 5a reduces to

$$f(v) = \int_{v_0}^{v'} (G_v - G_{v'})^{-\frac{1}{2}} dv' \quad (6)$$

From equation 2,  $\partial T / \partial J(J+1) = B_v$ ; and equation 5b becomes (for  $J=0$ )

$$g(v) = \int_{v_0}^{v'} B_{v'} (G_v - G_{v'})^{-\frac{1}{2}} dv' \quad (7)$$

The lower limit of integration,  $v_0$ , is defined by  $G(v_0) = -Y_{00}$  or the electronic energy (22:30-31). With the aid of a computer, equations 6 and 7 can be solved numerically. Once  $f$  and  $g$  are obtained, the turning points can be calculated (10:25 July). These are shown in equations 7 and 8.

$$R_{min} = \left( \frac{f}{g} + f^2 \right)^{\frac{1}{2}} - f \quad (8)$$

$$R_{max} = \left( \frac{f}{g} + f^2 \right)^{\frac{1}{2}} + f \quad (9)$$

Equations 6 and 7 also have physical significance on the potential energy curve. The  $f$  parameter is the half width of the potential at the energy level considered and  $2g$  is the midpoint of that energy level. Both of these parameters are

required to accurately position a vibrational level above the internuclear separation axis.

Once the turning points are calculated, the first-cut approximation of the potential is complete. However, because an infinite number of molecular constants can not be calculated equations 3 and 4 and therefore the energy equation itself must be truncated. This reduces the accuracy of the approximation as a whole. It is generally the upper states, which are closer together, that are affected the most by the truncation. One method used to increase the accuracy of the RKR approximation is the IPA approach. Using the values calculated by the RKR method as starting values, the potential can be recalculated through an iterative technique until it has the desired accuracy. Yet even this approach shows anomalous behavior at higher energy levels, especially on the inner branch of the potential energy curve (20:84).

As mentioned before, the IPA is an iterative method. The sequence of steps which are iterated are as follows (10:22 Aug):

- 1) Assume a function for the potential (the RKR value, for example)
- 2) Do the perturbation analysis and calculate the energy  $E$
- 3) Compare  $E(\text{calculated})$  with  $E(\text{measured})$
- 4) If the two values differ by more than a specified amount, calculate  $\Delta U$  due to this difference
- 5) Use  $\Delta U$  as a perturbation to the initial  $U$  and recalculate  $E(\text{calculated})$

Repeat steps one through five until the calculated energy value is within a specified amount of the measured energy value. At each iteration the potential is adjusted and

therefore it becomes more accurate as the energy values become more accurate.

The IPA begins with the assumption that a diatomic molecule can be modelled as a rotating vibrator. Evidence that this is true can be found in the fine structure of the rotation bands (15:106). The rotating vibrator can be described by the radial form of the Schrodinger Wave Equation shown in equation 10 (27:48).

$$(H_0 + H_{\text{rot}}) \Psi_{vj}(r) = E_{vj} \Psi_{vj}(r) \quad (10)$$

Here,  $E_{vj}$  is the energy eigenvalue (in units of  $\text{cm}^{-1}$ ) specified by the parameters  $v$  and  $j$ ;  $H_0$  is the Hamiltonian of the non-rotating molecule expanded below in equation 11 (for units of  $\text{cm}^{-1}$ ).

$$H_0 = \left[ \frac{-\hbar^2}{4\pi\mu c} \right] \frac{d^2}{dr^2} + U_0(r) \quad (11)$$

$\mu$  is the reduced mass of the molecule  
 $r$  is the internuclear distance  
 $U_0(r)$  is the potential of the rotationless molecule  
 $H_{\text{rot}}$  is the Hamiltonian for a rotating molecule.

The exact form of the Hamiltonian varies for each coupling case, but for a singlet sigma state it is (assuming the rigid rotor):

$$H_{\text{rot}} = \left[ \frac{\hbar^2}{4\pi\mu c} \right] \left[ \frac{J(J+1)}{r^2} \right] \quad (12)$$

This form of the Schrodinger Wave Equation is then numerically solved. Initially, the RKR potential is used for

$U_0(r)$ , but in succeeding iterations the new "perturbed" value of the potential is used.

$$U_0(r) = U_0^{(0)}(r) + \Delta U_0(r) \quad (13)$$

= "old value" + "calculated perturbation"

The solution of the Schrodinger Wave Equation yields the energy eigenvalue for the  $v$  and  $j$  being considered. This is the value which is then compared to the measured value and  $\Delta E_{vj} = E_{vj}(\text{measured}) - E_{vj}(\text{calculated})$  is calculated. This value is then checked against the convergence criteria. At this point the perturbation analysis is applied. The new potential difference is calculated from this  $\Delta E$ . Normally,  $\Delta U_0(r)$  is known and  $\Delta E_{vj}$  is the desired quantity.

$$\Delta E_{vj} = \langle \Psi_{vj}^0 | \Delta U_0(r) | \Psi_{vj}^0 \rangle \quad (14)$$

The value on the right hand side is the expectation value. The "inversion" occurs here because  $\Delta E_{vj}$  is known and  $U_0(r)$  is the desired quantity, which must be chosen to continue the evaluation. If the method is to converge rapidly, a well-behaved form of  $U_0(r)$  must be used. Good results, with the trade off of longer compiling times, have been achieved with a form of  $\Delta U_0(r)$  which is a summation of a Legendre Polynomial damped by an exponential function (27:50). It is this form of the potential which is used in the programs presented in this paper.

With the calculation of  $\Delta U_0(r)$  the Hamiltonian becomes,

$$H = H_0 + H_{\text{rot}} + \Delta U_0(r) \quad (15)$$

This Hamiltonian is now used in the Schrodinger Wave Equation which is solved numerically to get a new value of  $E_{vj}$  (calculated), and the iteration proceeds as usual. When the convergence criteria is met, the process is stopped. With the improved potential, more accurate wavefunctions can be calculated, and from them more accurate Franck-Condon Factors.

#### Franck-Condon Factors

The desired outcome from these calculations is a set of numbers between zero and one, one for each possible transition between vibrational levels of the two states. The closer the number is to one the larger the probability of that transition occurring, and therefore the stronger its intensity will be. Because of the normalization of the wavefunctions, the total of all Franck-Condon Factors for transitions from or to a specific vibrational level should be one. The process of calculating Franck-Condon Factors comes full circle when a spectroscopist uses a set of "raw" factors to justify the labelling of transitions in a spectrum used to calculate the constants which in turn are used to calculate the potentials that the factors are derived from.

The theory behind the math was originally proposed by James Franck in 1925 to explain the dissociation of iodine vapor (13:21). Edward Condon expanded Franck's principle and

applied it to intensity distributions in 1926. In 1928, Condon updated the principle to incorporate principles from the then new quantum physics (6:32). It is in this form that the principle now stands. The underlying concept of the Franck-Condon Principle is really quite simple. Because the mass difference between the nuclear material and the electrons is quite large, when the electron jumps from one electron state to another the transition takes place "so rapidly in comparison to the vibrational motion that immediately afterwards the nuclei still have very nearly the same relative position and velocity as before the 'jump'" (15:194). Or stated another way, the transition will be vertically upward or downward onto the potential energy curve of the second state. The strength of the transition will then be determined by how much time the electron spends at both the before and after location. In other words, the stronger transitions occur between locations of maximum probability for the electron. Classically, the electron spends most of its time at the minimum and maximum intersections of the vibrational level with the potential, as seen in Figure I. The most probable (most intense) transitions would occur where the upper turning point is vertically above the lower point as in transitions A and B. But in transition C, the upper turning point is vertically above the midpoint of the vibrational level of the lower state. Therefore C will be a weak (less probable) transition. To determine strengths of transitions quantum

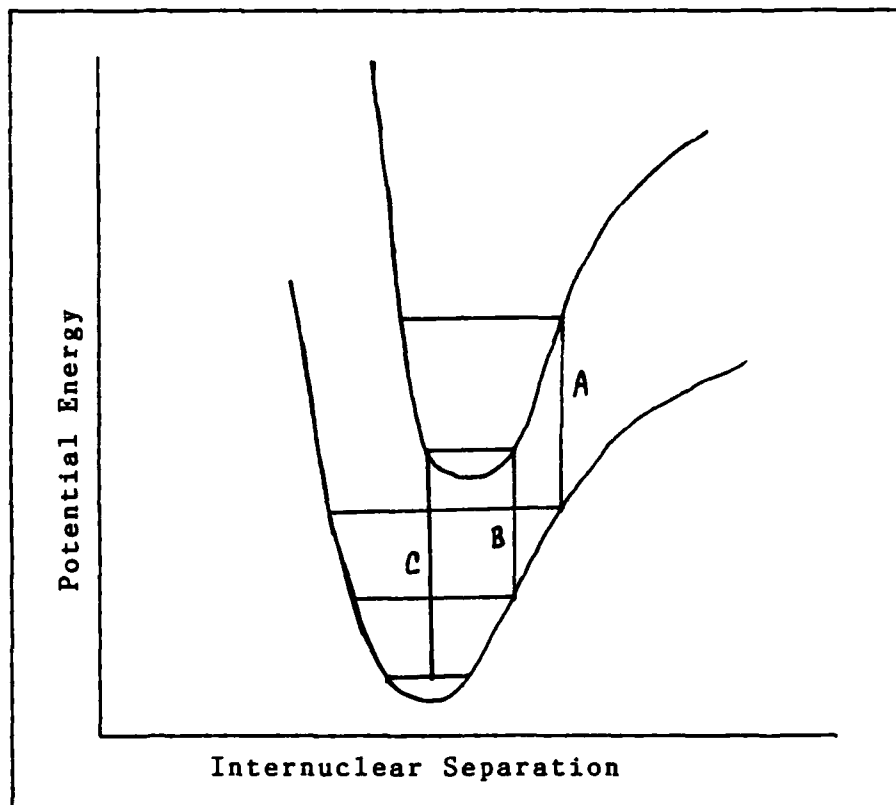


FIGURE I. Franck-Condon Principle (Classical)

mechanically, the wavefunctions for each vibrational level must be studied. As in the classical case, the most probable transition will occur when a maximum of the upper state lies vertically above a maximum of the lower state. As higher vibrational levels are considered, the points of maximum probability for the position of the electron shift towards the classical turning points. But because quantum mechanics is more concerned with the probability of electronic position rather than its actual location the value of the wavefunctions must be integrated over the entire vibrational level. The amount of overlap of the two levels of a transition is what then becomes important. There has even been some discussion in the literature (23) that mention of "vertical" transitions should be dropped from any description of the Franck-Condon Principle on a quantum mechanical level. In other words, the only statement necessary is one of the overlap integral. From this point of view, the transitions are no longer required to be vertical. The manner of overlap is also important. For maximum probability, the maximum of the upper and lower states should occur at the same separation of the two molecules. A minimum on one level will cancel out a maximum on the other. The product of the two vibrational wavefunctions integrated across their overlap and squared is the Franck-Condon Factor (18).

The Franck-Condon Factor can also be derived from a quantum mechanical statement of the transition moment between an upper state  $v'$  and a lower state  $v''$ . The probability of

the transition occurring (known as the Einstein Coefficient) is directly proportional to the square of the transition moment (also known as the electric moment). The transition moment is a function of the dipole moment (M); a vector whose components are the sum of each charge multiplied by its distance from the origin (15:199). The transition moment is shown in equation 16.

$$R = \int \Psi'^* M \Psi'' d\tau \quad (16)$$

By referring to the Born-Oppenheimer Approximations and ignoring rotational effects, the two molecular wavefunctions can be split into a vibrational and an electronic part. That is,  $\Psi = \Psi_e * \Psi_v$ ; this is possible because the nuclear motion is much slower than electron motion in the molecule and thus the wavefunction describing a particular vibrational level of an electronic state can be broken down into the product of two wavefunctions, one purely for the electronic state, the other for the vibrational level under consideration. Each of the separated wavefunctions is now dependent upon independent coordinate systems, one for the electrons, the other for the nuclear components (17:231). Similarly, the dipole moment, M, can be broken down into the sum of a nuclear part based on nuclear coordinates and an electronic part based on the electron coordinate system,  $M = M_e + M_n$  (15). Both expanded equations can then be substituted back in equation 16. Because the vibrational wavefunction is real, its complex conjugate is identical to the original wavefunction. This

fact and the expanded form of 16 allow the transition moment to also be written as a sum of an electronic and nuclear part as in equation 17.

$$R = \int M_e \psi_e' \psi_e'^* \psi_v' \psi_v'' d\tau_e + \int M_n \psi_e' \psi_e'^* \psi_v' \psi_v'' d\tau_n \quad (17)$$

Looking at the second term and remembering that the two coordinates, electronic and nuclear, are independent of one another, the integral can be rewritten as:

$$\int M_n \psi_v' \psi_v'' d\tau_n \int \psi_e' \psi_e'' d\tau_e \quad (18)$$

The second integral in equation 18 has a value of either zero or one. The set of electronic wavefunctions is orthonormal and the integration of their product from plus to minus infinity, will have a value of one if  $\psi_e' = \psi_e''$  and zero if  $\psi_e' \neq \psi_e''$ . If the former were true no transition would have occurred, therefore the value of the integral and further, the entire second term is zero.

The first term can also be split into the product of a nuclear and electronic part. The equation for the transition moment reduces to the form in equation 19.

$$R = \int \psi_v' \psi_v'' d\tau_n \int M_e \psi_e' \psi_e'^* \psi_e'' d\tau_e \quad (19)$$

The second integral is known as the electronic transition moment,  $R_e$ . This factor does depend on internuclear distance but here the Franck-Condon Principle is brought into play. A restatement of the principle is that  $R_e$  varies slowly with internuclear distance and therefore may be replaced by a

constant value  $\bar{R}_e$ . The constant value can then be pulled out of the integral and the transition moment becomes:

$$R = \bar{R}_e \int \psi'_v \psi''_v d\tau_n \quad (20)$$

The remaining integral should be recognized as the overlap integral, and its square as the Franck-Condon Factor (10:26 Sept). The approximation made earlier, of the Franck-Condon Factor being proportional to the transition probability is valid only as long as  $\bar{R}_e$ , which is also known as the R centroid, remains constant. There are some who believe this approximation is not accurate enough and attempts have been made to calculate directly the fluctuation of  $R_e(r)$  with  $r$  (4:77, 18:95). It was hoped that gains would be made in three areas: a form of  $R_e(r)$  vs  $r$  would be found, intensities of unmeasured bands could be calculated, and experimental data obtained from several measurements could be more easily smoothed (16:20). This area of study known as the R Centroid Approach has generally met with good but limited results (the method does not accurately describe highly quantum transitions, i.e. transitions not classically allowed). This approach has been criticized by Thomas James (16) who concluded that the R Centroid Approach may be "an unsatisfactory method of treating experimental data in many cases".

Returning to the overlap integral, because the vibrational wavefunctions represent different electronic states they are not an orthonormal set, and the integral will

have a value other than zero or one. Each wavefunction is normalized however; and has a maximum value of one. Therefore the maximum value for the integral is one and in general, it will vary between zero and one. The evaluation of this integral is the key to a computer calculation of Franck-Condon Factors. A compromise must be reached between accuracy of the method and the computer time required to implement it. A Simpson's Rule approximation to the overlap integral was sufficient for the calculations in this work (see equation 21).

$$\int \psi_u^* \psi_l dx \approx \sum_i \frac{\Delta x}{3} [(\Delta \psi_i^* \Delta \psi_{i+1}) + 4(\Delta \psi_{i+1}^* \Delta \psi_{i+2}) + (\Delta \psi_{i+2}^* \Delta \psi_{i+3})] \quad (21)$$

Here the  $\Delta \psi_i$ 's represent the product of the upper and lower wavefunction values at location 'i'. In other words,  $\Delta \psi_i = \Delta \psi_i^l * \Delta \psi_i^u$ . Simpson's Rule improved accuracy over the previous method, a histogram integral approximation, but did not noticeably increase the run time of the program.

### III. COMPUTER PROGRAMS

#### Program RKR-IPA

The potential modelling program, RKR-IPA, was written by Dr C.R. Vidal in Fortran IV to run on a Cray-1 computer. The program was brought to AFIT and altered to run on available systems in 1983 by Capt Lyle Rutger as a part of his thesis project. The program was changed to Fortran V and the arrays were decreased in size to meet memory requirements for the CDC Cyber located at Wright-Patterson AFB. Other modifications were made to the program to update the code and conform its output to Rutger's uses. The program calculates an RKR potential and contains an optional IPA routine which increases the accuracy of the potential approximation. Input to the program is in the form of a data file containing all the necessary information to run the program. The RKR-IPA program is not currently set up to run interactively. Simple modifications would allow this to be done, but because of the large amount of output generated by the program it has been kept in its batch configuration. The RKR-IPA program also produces two computer files. The first is a file referred to as "POINTS" in the program. This file contains the turning points for each vibrational level of the potential. POINTS is used as input to the plotting program (CRVPLT) written by Pow. The second file created is called "WAVE" and is of primary importance to the calculation of the Franck-Condon Factors. WAVE can be broken down into several sections, its

first two lines cover general information about the potential as a whole. Line one shows the highest vibrational level for which a wavefunction has been calculated; line two contains the minimum and maximum internuclear distances over which the potential has been calculated. The third number on line two is the number of points at which the wavefunction has been evaluated. The remainder of the file is composed of tabulated values of the wavefunctions for each vibrational level in the following format. The first line of each section contains information about a specific level and has three numbers on it. The first is the vibrational level of the section (starting at zero), the second is the array location of the first non-zero (greater than  $1 \text{ E-}8$ ) value of the wavefunction, and the third is the array location of the last non-zero value of the wavefunction. These last two numbers are referred to as the start/stop indices in the program documentation. The next N lines, where N is the number of points given in line two, contains the tabulated values of the wavefunction. One value for each array location which corresponds to an internuclear distance through a scaling factor. This same pattern, one line of information followed by N lines of wavefunction values, is repeated for the rest of the file. The final section is for the highest vibrational level referred to in line one of the file.

An example of the input data file is shown in Figure II. It contains all of the information needed by the program to

```

1.) 1
2.) POTENTIAL OF THE PBO MOLECULE (TOTAL FIT)
3.) LARGE B STATE
4.) 1 0.159994000D+02 0.203973000D+03
5.) 3 3 2 1 0
2.228500000D+04 4.980000000D+02 -2.200000000D+00
0.264600000D+00 -0.002600000D+00
0.300000000D-06
6.) 8.7643000D+03 2.228500000D+04
7.) 15.00 0.25
8.) 0
9.) 0.60 4.50 0
10.)
11.) 0 0
12.) 1
13.) 0 0 10 20 1.D+00
14.) 0.6 4.1 451 4 10 0 0
15.) 1 12 6 1 12 42 1 12 110 1 12 210 1 12 306 1 10 420
1 8 552 1 8 702 1 6 812 1 4 930 1 16 0
16.) 0

```

Figure II. RKR-IPA Input Data File

model the potential and allows the selection of all available options. It also indicates how many vibrational levels will be calculated. The information is presented in the following format (the numbers correspond to the lines indicated in the figure):

1. The first line should have a one in column one to insure the program will execute rather than just list. Using the /NOSEQ command in the jobfile used to submit the batch job will insure that the first column of the data file is processed by the computer. Without this command, the computer will assume the first several spaces contain line numbers and it will not process any information contained in these spaces.

2. The second and third lines indicate the molecule and state to be investigated.

3. The fourth line contains the mass scale to be used and the masses of the two atoms. A one in column four indicates the masses are in the Carbon-12 scale, a two indicates oxygen-16. The masses are entered next with a 2D16.9 format. The reduced mass of the molecule may be used instead of the individual masses by entering it with the same format in place of the first mass and leaving the second mass blank.

4. The number of Dunham Coefficients presented is covered in the next line. Format is 4I5. The first number is the number of lines containing coefficients, the remaining numbers give the number of coefficients in each line. For

example, a common sequence is 3, 3, 2, 1. This would be interpreted as three lines of coefficients follow, three coefficients on the first line ( $T_e, \omega_e, \omega_e X_e$ ), two on the second ( $B_e, \alpha_e$ ), and one on the third ( $D_e$ ).

5. Enter the constants as described in point 4. Format is D18.9.

6. The next line after the final Dunham Coefficient(s) contains the dissociation energy and the term energy. Format is 2D15.8.

7. Next, indicate the highest vibrational level to be investigated, and follow by the incremental step size used in calculating the turning points. Format is 2F6.2.

8. If the values of the Klein Action Integral are to be printed, the first column of the next line should contain a one. A zero will skip printing the values.

9. If Vidal's extension routine is to be used to extend the curve past the normal range of the program, an extended internuclear range must be defined. This range should be large enough to contain the minimum and maximum internuclear separation represented by the extended potential well. The format for these two separations is 2F6.2. The final number on the line is the number of extra data points used for the extension. This number must be between 0 and 25, with a format of I2.

10. If the last number on the previous line is anything other than zero, the data points are entered on this line as described in Rutger's thesis (22:B-9). Otherwise the line is

left blank.

11. The next line should contain two zeroes, format 2I2. This line is a hold over from when the program punched an output deck. Since Rutger changed the PUNCH commands to comment lines, that option is no longer available without modifying the program. A zero suppresses punching the card decks.

12. If the IPA routine is desired this line should contain a 1 in column one. A zero will skip the IPA and repeat the RKR analysis on the next set of data. If no further data is given, this line should be followed by a zero on a separate line.

Note: The following data lines are needed only if the IPA option is selected.

13. A one in column four on this line will print every iteration of the function SCHR (the function subroutine which solves the Schrodinger Wave Equation), a zero will suppress printing. A one in column eight will print the wavefunction value at every Nth point, where N is given by the third number on the line. A zero in column eight will not print the values. Columns nine through twelve are for N which defines how many values of the wavefunction will be printed. The next four columns are for the number of iterations SCHR will complete in an attempt to find a converging solution. Finally, enter the convergence criteria for the Schrodinger Wave Equation with a D10.0 format.

14. Next, define the range of internuclear separations

over which the Schrodinger equation will be analyzed. Format is 2F10.1, the values are in units of angstroms. The first number represents the first position of the wavefunction array (minimum internuclear separation) and the second number represents the last position of the array (maximum separation). Beginning in column 21 enter the number of elements in the wavefunction arrays, (that is, the number of points at which the wavefunction will be evaluated) with an I5 format. The maximum number is 2403. Beginning in column 26 with an I5 format enter the number of iterations of the IPA routine to be performed. Starting in column 31 enter the number of terms to be used in the Legendre polynomial, format I5. This is part of the chosen function used for  $\Delta U_0(r)$ . Next, place a zero in column 36. This is another hold over from output punched on card decks. Finally, in column 40 should come a zero if only the first and last iterations of IPA are to be printed, or a one if all iterations should be printed.

15. The next two lines contain eleven sets of three number groups which define the range of vibrational and rotational levels to be studied. The first line contains six sets, the second five. Each group has a format for the three numbers of: I2, I3, F7.0. The order within the group is, minimum  $V+1$  level, maximum  $V+1$  level,  $J(J+1)$  value. Note that the range of vibrational levels studied for a particular  $J(J+1)$  value are entered as  $V+1$  values, not  $V$ . The last group of three numbers on these two lines must have  $J(J+1) =$

0 so that the rotationless potentials will be evaluated. If the number of vibrational levels calculated and read to the file WAVE is to be changed, the new V level must be shown both in the final group of numbers in these two lines and in the first number described in point 7. The maximum  $v+1$  level for the rotationless group ( $J(J+1)$ ) should be the highest vibrational level called for in these two lines. This will ensure that when the file WAVE is created it will contain exactly the number of vibrational levels desired, and no extra ones.

16. The last line must contain a zero to halt execution of the program.

The most frequent changes to the data file for a particular electronic state are to the number of  $v$  levels calculated and the number of points at which the wavefunctions are evaluated. The lines which must be altered are covered under points 14 and 7 for the former and point 13 for the latter. For a thorough explanation of the variables represented in the data file and the calculations done in the RKR-IPA program please refer to Rutger's thesis, Appendix B (22:B-1). For a program listing of the RKR-IPA code refer to Pow's thesis, Appendix B.

#### Program FCFACT

Program FCFACT was written by Capt Pow in Fortran V to calculate Franck-Condon Factors from wavefunction values calculated by the RKR-IPA program. FCFACT uses the files

created by two RKR-IPA runs as input, one for the upper electronic state and the second for the lower. Before any calculations can take place, the potentials must be checked to insure proper overlap and scaling. The scaling factor (angstroms per array location) is calculated in line 720 for the upper molecular state and in line 730 for the lower. If the scaling of the two states differs by more than a specified amount, the lower state is rescaled to match the upper state. The method of rescaling is described in Pow's thesis (20:44-47). Once the scaling has been adjusted, the overlap of the two states is checked, and corrected if necessary. Once again, the values of the lower wavefunction are shifted to match the upper. The purpose of this operation is to insure that matching array locations represent the same internuclear separation. The shift subroutine is described on page 47 of Pow's thesis (20:47). Finally, the wavefunctions of both states are normalized so that the sum of the squares of the wavefunction values for one vibrational level equals one. Pow discusses the normalization subroutine on page 48 of his thesis (20:48). After these three processes have been completed, the wavefunctions are properly prepared to begin calculation of the Franck-Condon Factors.

The calculation of Franck-Condon Factors involves a multiplication of the values of two wavefunctions, one from the upper state of the transition and one from the lower state, plus an integration across the region where the two

states overlap. The result is then squared to give the desired quantity. This process is carried out for each possible combination of upper and lower vibrational level. Originally the integral was approximated by a histogram. The values at each array location of the two wavefunctions were multiplied together and the individual products were summed. The start and stop locations of the region of overlap were determined from the start/stop indices before beginning the integration. Once the final pair of values was multiplied and summed, the number was squared and stored in an array called FACTOR. Once all of the Franck-Condon Factors were calculated the array was printed out. FCFACT has been revised for this thesis, to use a Simpson's Rule approximation of the integral. The loop which integrates and calculates the Franck-Condon Factors falls between lines 870 and 1100 in the program. First, the tabulated values of the wavefunctions for the two vibrational levels of interest are multiplied at matching array locations and the product stored in an array named WFXN. The Simpson's Rule approximation is carried out on this array and makes use of a conventional code (24). Because of the speed of the approximation, the integration is carried out over the entire product array which has the same length as the shorter of the two wavefunction arrays, rather than just over the non-zero overlap of the two wavefunctions. Because of the tabulated nature of the wavefunction values, the  $\Delta x$  required in the Simpson's Rule approximation (see equation 21) is not the

scaling factor SCALUP, but one. This is because the approximation steps through the array using each element in the calculation. As before, the final value of the integral is squared and stored in the FACTOR array, to be printed out after all values have been calculated. The Simpson's Rule approximation was verified by comparison with a set of values known to be correct. These values were calculated by the earlier histogram version of FCFACT from a set of test data initially used to insure the program was producing accurate numbers.

Several changes must be made to program FCFACT in order to prepare it to calculate the Franck-Condon Factors for a specific molecular transition. The arrays in the program must be dimensioned to hold the required number of elements. The first dimension is for the vibrational levels and begins with zero, the second represents the number of points and begins with one. The simplest way to avoid having to re-dimension all the arrays before every run is to find a reasonable combination of V levels and points which is larger than or equal to the values in the runs to be made. These numbers need not be changed until a larger run is required. All of the changes described below must be made internal to the program and can be done using the line or screen editor available on the operating system of the CDC Cyber. The two wavefunction arrays must be identically dimensioned for the program to run. Once the arrays are correctly dimensioned, the corresponding DATA statements must be updated to insure

that each array location will be initialized to zero. The large numbers in the DATA statements represent the total number of elements in the array, calculated by multiplying the first array dimension ( $V+1$ ) by the second (number of points). These DIMENSION and DATA changes must be made the entire length of the code, wherever the appropriate statements or numbers are found, the subroutines also contain several arrays which must be changed. Next, the names of the files opened in lines 380 and 390 must be changed to the names of the files containing the wavefunction values for the two states in the transition of interest. The lower state must always be opened under unit 7 and the upper under unit 8. Finally, the header for the matrix of Franck-Condon Factors must be changed to show the correct transition and any other pertinent information. Program FCFACT in its present form can be run interactively, if the local directory containing the compiled version of the program also contains the two input data files. An interactive run can be a useful debugging tool if available options on the Fortran V compiler are used. Compiling the program with these debugging options chosen and then running it interactively can point out errors more quickly than waiting for the paper output from a batch job. The code for the updated portion of FCFACT is contained in Appendix A of this thesis.

#### IV Results and Analysis

Franck-Condon Factors were calculated for six molecules, lead oxide and five halogen or interhalogen compounds ( $\text{Br}_2$ ,  $\text{BrCl}$ ,  $\text{BrF}$ ,  $\text{ICl}$ ,  $\text{IF}$ ). The molecular constants for lead oxide were calculated from data collected during spectroscopic observation in the lab at AFIT. The potentials and wavefunction values were calculated for nine states of  $\text{PbO}$  (a, b, A, B, C, C', D, E, X) and Franck-Condon Factors were calculated for the transition from each state to ground, plus the D to a and A to a transitions. The B to X transitions of this molecule were used as the test data for initial verification of the programs and all modifications. The molecular constants for the halogens were drawn from the open literature. The number of potentials, wavefunctions, and transitions vary for each halogen. The results for each molecule follow, with lead oxide first and then the halogens in alphabetical order.

##### Lead Oxide

Lead oxide was thoroughly investigated in a previous thesis (20) using constants calculated by Rutger (22:54) and from the open literature. RKR-IPA and FCFACT were run using those values to insure valid copies of the programs had been obtained. The test run used the data for the B and X states of  $\text{PbO}$  and calculated 15 vibrational levels for each. The results were verified by comparison with the values Pow

obtained. Next, the programs were rerun using the same data, calculating the wavefunction values and Franck-Condon Factors for 24 vibrational levels. The programs were again run for 24 levels using the new molecular constants calculated by Capt Jeff Duray and presented in his thesis (11). The Franck-Condon Factors from the two sets of data were compared for each transition with the largest change being seen in the higher vibrational levels. This was expected, as the purpose of the new investigation of lead oxide was to increase the accuracy of the constants for the higher levels. The Condon Parabola is a characteristic feature of tables of Franck-Condon Factors, shown by two lines of intensity maxima in the table. These are due to the fact that there will be two values of maximum probability for each level of the beginning state in the transition, one for each turning point of that level, see Figure I. Theoretically, these two lines will form a parabola (15:196-198). The Condon Parabola for the new data shows only minor deviations from the older parabola and these are for  $v > 10$ . For  $v < 10$  the two parabolas coincide exactly. The two sets of Franck-Condon Factors, for the region of the parabola, are shown in Table 1. The first value is the value calculated by Pow using a simple Histogram approach. The second is the value calculated using Duray's molecular constants and the same Histogram approach. The third entry is the absolute difference between Franck-Condon Factors calculated using in one case the simple Histogram approach and in the second case the more accurate Simpson's

TABLE 1

Comparison of Franck-Condon Factors: PbO B-X transitions

V"	0	1	2	3	4	5	6	7	8	9	10	11
V'	49	160	244	235	165	90	39	14	4	1	0	0
0	48	161	246	237	164	88	38	13	4	1	0	0
	0	0	0	0	0	0	0	0	0	0	0	0
	126	196	73	1	79	166	168	112	53	19	5	1
1	124	194	73	1	80	168	169	112	53	19	5	1
	0	0	0	0	0	0	0	0	0	0	0	0
	176	90	6	112	86	3	45	139	159	109	51	18
2	176	90	6	110	87	3	45	139	159	109	52	18
	0	0	0	0	0	0	0	0	0	0	0	0
	178	9	85	69	3	90	74	2	47	136	148	95
3	182	9	84	68	3	89	75	2	47	135	147	95
	0	0	0	0	0	0	0	0	0	0	0	0
	150	8	101	0	80	44	9	89	54	0	65	140
4	154	9	99	0	79	43	9	89	54	0	64	138
	0	0	0	0	0	0	0	0	0	0	0	0
	111	45	49	37	63	5	80	18	28	89	29	8
5	113	48	46	38	61	6	79	17	28	89	29	7
	0	0	0	0	0	0	0	0	0	0	0	0
	76	75	7	79	5	64	24	28	68	1	56	75
6	76	80	5	77	4	64	23	29	66	1	55	75
	0	0	0	0	0	0	0	0	0	0	0	0
	49	84	2	67	14	59	7	66	1	59	37	8
7	48	89	4	62	15	56	7	65	1	57	37	7
	0	0	0	0	0	0	0	0	0	0	0	0
	30	76	19	31	52	12	54	14	40	36	12	67
8	29	81	25	25	52	10	53	14	40	35	11	66
	0	0	0	0	0	0	0	0	0	0	0	0
	18	61	35	6	65	2	57	7	54	2	60	4
9	18	65	45	3	61	3	53	7	53	2	58	4
	0	0	0	0	1	0	1	1	0	0	0	0
	11	46	43	0	49	26	22	45	11	43	16	31
10	11	49	55	2	42	29	17	43	10	43	16	30
	0	0	0	0	0	0	0	0	0	0	0	0
	7	33	43	5	26	46	1	57	4	47	5	49
11	7	36	56	13	17	49	0	50	5	45	6	48
	0	0	0	0	0	0	0	0	0	0	0	0

Order of entries: FC Factors using data from source 11  
 FC Factors using data from source 20  
 Absolute change in source 11 factors  
 when FCFACT upgraded to Simpson's Rule

TABLE 1 (cont.)

Comparison of Franck-Condon Factors: PbO B-X transitions

v"	12	13	14	15	16	17	18	19	20	21	22	23
v'	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0
2	5	1	0	0	0	0	0	0	0	0	0	0
	5	1	0	0	0	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0
3	43	15	4	1	0	0	0	0	0	0	0	0
	44	15	4	1	0	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0
4	133	79	33	11	0	0	0	0	0	0	0	0
	132	79	34	11	1	0	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0
5	90	142	115	61	7	1	0	0	0	0	0	0
	87	140	115	63	8	2	0	0	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0
6	7	30	115	137	42	14	3	1	0	0	0	0
	8	27	110	136	46	17	4	1	0	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0
7	77	46	1	65	123	68	26	7	1	0	0	0
	76	48	0	57	124	75	32	10	2	0	0	0
	0	0	0	0	0	0	0	0	0	0	0	0
8	6	36	77	15	105	139	98	44	14	3	1	0
	8	33	78	19	91	134	105	54	20	5	1	0
	0	0	0	0	0	0	0	0	0	0	1	0
9	46	43	2	67	0	59	135	125	68	25	6	1
	42	46	1	62	1	41	119	127	81	35	11	3
	0	0	0	0	0	0	0	0	0	0	0	0
10	39	7	62	10	77	16	18	107	142	95	41	12
	39	5	61	14	75	26	6	81	132	108	56	20
	0	0	0	0	0	0	0	0	0	1	0	0
11	1	56	6	39	1	66	51	0	64	141	122	63
	1	53	7	34	0	55	61	3	37	116	128	82
	0	0	0	0	0	0	0	0	0	0	0	0

Order of entries: FC Factors using data from source 11  
 FC Factors using data from source 20  
 Absolute change in source 11 factors  
 when FCFACT upgraded to Simpson's Rule

Rule approximation to the integral (both with Duray's data). The PbO B to X transition was again used as the test case for this modification to the program FCFACT.

All of the states for PbO presented in this thesis were calculated from the more recent data, which is presented in Table 2. The values of the wavefunctions, except for the E state, were calculated for a total of 25 levels (beginning at zero) and evaluated at 301 points on each vibrational level. It is important to stay within the accurate portion of the potential energy curve when extending the number of levels calculated. The potential approximation begins to break down near the dissociation energy and special procedures need to be undertaken to maintain the desired level of accuracy in this region. For all states of PbO except the E state, level 24 is within the reliable region. The Franck-Condon Factors for each of the excited states to the ground state follow in Tables 3 through 10. The factors for the two transitions between excited states calculated, A to a and D to a, are included in Tables 11 and 12 respectively. The E state has the highest potential energy of all the PbO excited states and is very wide and shallow. The state is difficult to calculate and the maximum vibrational level accurately attainable is 15. Because of the overlap between the E and the X states and because of the requirements of the program FCFACT, a minimum of 351 points were required to give a valid calculation of the Franck-Condon Factors for the transitions between these two states.

TABLE 2  
Data for Lead Oxide  
Part I.

STATE	a	b	A	B
$T_e$	16031.1	16335.4	19876.2	22303.6
$\omega_e$	483.404	433.468	445.199	491.732
$\omega_e X_e$	2.711	-0.036	0.779	0.980
$B_e$	0.252	0.255	0.25869	0.2646
$\alpha_e$	.0016761	---	.00138	.0026
$D_e$	2.2 E-7	---	3.3 E-7	3.0 E-7
Dis. En.	14865.7	14436.8	11254.7	8764.3

All values in inverse centimeters  
First three constants from source 11. All others from  
source 20.

TABLE 2  
Data for Lead Oxide  
Part II.

STATE	C	C'	D	E	X
$T_e$	23794.6	24941.9	30059.3	34443.0	0
$\omega_e$	550.550	500.884	617.682	477.414	722.687
$\omega_e X_e$	5.458	3.402	9.556	12.964	3.613
$B_e$	0.254	0.248	0.2711	0.239	0.307519
$\alpha_e$	0.002	0.0018	0.0031	0.0014	0.001967
$D_e$	2.5 E-7	2.5 E-7	2.8 E-7	2.8 E-7	2.2 E-7
Dis. En.	14889.8	13762.8	8511.1	4414.0	31214

All values in inverse centimeters  
The first three constants are from source 11. All  
others are from source 20.

TABLE 3

Franck-Condon Factors for PbO Small A to X Transitions

$v''$ $v'$	0	1	2	3	4	5	6	7	8	9	10	11
0	005	033	091	160	202	195	149	092	045	018	006	002
1	025	096	151	114	028	003	065	139	156	118	065	028
2	060	138	093	005	033	097	065	004	028	107	144	117
3	101	121	013	033	085	024	010	076	067	006	024	101
4	133	064	008	079	023	016	071	023	010	074	056	002
5	146	014	053	048	005	064	016	020	064	011	021	076
6	139	001	076	004	049	029	012	057	004	035	053	001
7	118	020	055	010	054	000	052	009	029	042	001	052
8	092	051	020	044	018	030	029	012	045	000	046	018
9	066	076	001	057	000	049	000	045	005	034	021	013
10	045	086	007	040	019	027	019	027	012	034	004	043
11	029	082	030	014	043	002	042	001	039	002	036	007
12	018	070	054	000	045	006	031	013	024	014	025	010
13	011	054	069	007	026	029	006	035	001	035	000	035
14	006	038	071	028	006	041	002	030	010	021	016	016
15	003	025	064	049	000	032	019	009	030	001	032	000
16	002	015	051	061	012	013	035	000	029	009	017	018
17	001	009	037	063	031	001	033	012	010	027	000	029
18	000	005	024	056	049	004	018	029	000	027	009	013
19	000	002	015	045	058	019	003	032	009	010	025	000
20	000	001	009	033	057	037	001	020	024	000	025	009
21	000	000	005	022	050	050	011	006	029	006	010	023
22	000	000	002	013	039	055	027	000	021	020	000	023
23	000	000	001	008	028	051	042	006	008	027	005	010
24	000	000	000	004	018	043	050	020	000	021	017	000

Values in the table are (FCF x 1000)

TABLE 3 (cont.)

Franck-Condon Factors for PbO Small A to X Transitions

v'' v'	12	13	14	15	16	17	18	19	20	21	22	23
0	000	000	000	000	000	000	000	000	000	000	000	000
1	010	003	001	000	000	000	000	000	000	000	000	000
2	067	029	010	003	000	000	000	000	000	000	000	000
3	136	108	060	025	002	000	000	000	000	000	000	000
4	034	108	130	095	018	005	001	000	000	000	000	000
5	038	000	054	120	078	035	012	003	001	000	000	000
6	040	071	017	010	128	106	058	023	007	001	000	000
7	032	003	060	053	035	109	125	084	038	013	003	001
8	015	056	008	023	026	004	071	126	108	059	022	006
9	046	001	039	039	052	057	003	031	107	125	082	036
10	001	037	023	009	011	020	068	025	005	075	127	105
11	027	023	009	044	037	037	001	053	052	001	039	114
12	031	003	039	001	021	010	051	007	025	066	017	012
13	001	034	005	027	011	040	000	041	029	004	059	041
14	017	018	013	026	036	000	039	013	018	047	001	038
15	031	001	032	000	001	032	011	020	032	002	047	016
16	010	022	008	023	020	016	013	029	003	041	003	031
17	001	026	004	024	026	003	031	000	035	002	032	019
18	019	005	025	002	001	028	002	028	005	025	016	014
19	026	003	020	009	013	013	015	015	013	020	008	030
20	010	020	002	025	025	001	025	002	027	001	030	000
21	000	023	005	015	007	020	004	023	002	025	003	026
22	008	008	020	000	001	020	006	016	010	014	012	015
23	021	000	020	007	017	002	022	000	023	001	024	002
24	021	008	006	020	020	005	013	012	007	018	003	022

Values in the table are (FCF x 1000)

TABLE 4

Franck-Condon Factors for PbO Small B to X Transitions

$v''$ $v'$	0	1	2	3	4	5	6	7	8	9	10	11
0	016	066	138	192	201	167	113	063	029	011	003	001
1	073	164	151	056	000	038	112	148	127	078	036	013
2	160	150	019	023	095	076	010	015	087	134	117	070
3	223	041	029	097	027	010	075	066	006	022	095	128
4	221	003	102	021	027	076	015	018	076	044	000	046
5	163	082	054	019	074	003	042	056	001	042	070	015
6	091	164	000	080	007	046	041	004	059	023	009	066
7	039	165	063	036	030	047	005	058	006	033	048	000
8	012	106	152	003	066	000	058	004	039	029	008	055
9	002	045	157	084	011	047	014	035	026	014	046	000
10	000	012	094	161	023	040	015	040	010	043	001	047
11	000	001	034	140	124	000	049	000	050	000	044	003
12	000	000	006	068	164	071	008	037	007	043	005	033
13	000	000	000	017	107	159	028	022	017	023	027	017
14	000	000	000	001	036	141	133	006	030	004	038	012
15	000	000	000	000	004	061	163	100	000	028	000	046
16	000	000	000	001	000	010	088	169	068	002	020	005
17	000	000	000	001	002	000	018	113	164	043	006	011
18	000	000	000	000	001	003	000	028	133	151	026	008
19	000	000	000	000	000	003	004	000	040	147	135	014
20	000	000	000	000	000	001	005	006	000	051	157	118
21	000	000	000	000	000	000	002	008	007	001	062	161
22	000	000	000	000	000	000	000	003	012	009	002	071
23	000	000	000	000	000	000	000	000	005	016	011	003
24	000	000	000	000	000	000	000	000	001	008	021	013

Values in the table are (FCF x 1000)

TABLE 4 (cont.)

Franck-Condon Factors for PbO Small B to X Transitions

$\nu''$ $\nu'$	12	13	14	15	16	17	18	19	20	21	22	23
0	000	000	000	000	000	000	000	000	000	000	000	000
1	004	001	000	000	000	000	000	000	000	000	000	000
2	031	010	003	001	000	000	000	000	000	000	000	000
3	100	053	020	006	000	000	000	000	000	000	000	000
4	113	118	076	033	002	000	000	000	000	000	000	000
5	012	084	123	095	016	004	001	000	000	000	000	000
6	040	000	053	117	061	022	005	001	000	000	000	000
7	044	059	005	028	120	074	028	006	001	000	000	000
8	011	021	065	018	091	126	085	032	007	001	000	000
9	045	027	006	060	003	077	130	093	036	008	001	000
10	007	028	041	000	044	000	066	132	100	039	008	001
11	036	020	012	048	038	051	000	057	135	107	041	007
12	015	021	032	003	008	028	056	002	052	138	112	041
13	018	027	009	039	043	014	019	058	004	048	142	115
14	027	007	035	002	001	037	021	013	058	005	048	147
15	003	032	001	038	038	005	031	025	010	058	006	051
16	046	000	032	000	001	034	009	026	028	008	057	005
17	015	041	001	028	034	004	029	012	022	029	007	055
18	004	027	034	004	007	030	007	025	015	019	030	006
19	009	000	038	026	017	012	026	009	022	016	018	029
20	007	008	001	046	011	012	016	023	011	019	017	018
21	100	004	006	004	015	012	008	019	020	012	017	017
22	160	084	002	004	055	012	013	005	022	019	012	016
23	079	155	070	001	015	058	009	012	003	025	019	011
24	004	084	147	057	001	021	060	008	011	002	026	019

Values in the table are (FCF x 1000)

TABLE 5

Franck-Condon Factors for PbO Large A to X Transitions

$v''$	0	1	2	3	4	5	6	7	8	9	10	11
$v'$												
0	026	097	179	218	197	141	082	039	015	005	001	000
1	091	180	127	022	009	083	148	149	104	054	022	007
2	165	129	004	051	108	049	000	048	122	139	101	053
3	204	028	046	095	011	029	090	047	000	048	119	129
4	190	003	102	013	040	074	005	035	082	030	003	065
5	143	058	058	020	074	001	051	052	000	053	070	011
6	090	116	003	077	011	043	044	004	062	025	010	069
7	049	131	017	061	015	058	001	058	012	026	057	003
8	024	108	070	010	064	006	049	019	024	046	000	052
9	010	072	106	006	056	016	044	009	049	000	050	013
10	004	041	105	047	012	058	002	051	004	042	014	024
11	002	020	080	087	003	050	019	030	021	029	013	039
12	001	009	051	098	036	012	054	000	048	000	044	000
13	000	004	028	081	075	002	043	024	017	033	010	032
14	000	001	013	055	090	032	009	052	001	039	008	031
15	000	000	006	032	079	068	003	035	031	006	039	000
16	000	000	002	016	056	084	031	005	048	007	026	021
17	000	000	001	007	033	075	064	004	026	037	001	038
18	000	000	000	003	017	054	078	033	002	043	015	014
19	000	000	000	001	008	033	070	062	007	018	040	001
20	000	000	000	000	003	018	051	073	035	000	036	023
21	000	000	000	000	001	008	032	065	061	011	011	040
22	000	000	000	000	000	004	017	047	069	039	000	028
23	000	000	000	000	000	001	008	029	060	060	016	005
24	000	000	000	000	000	001	004	016	043	065	042	002

Values in the table are (FCF x 1000)

TABLE 5 (cont.)

Franck-Condon Factors for PbO Large A to X Transitions

$v''$	12	13	14	15	16	17	18	19	20	21	22	23
$v'$												
0	000	000	000	000	000	000	000	000	000	000	000	000
1	002	000	000	000	000	000	000	000	000	000	000	000
2	021	007	002	000	000	000	000	000	000	000	000	000
3	088	044	017	005	000	000	000	000	000	000	000	000
4	123	116	072	032	003	001	000	000	000	000	000	000
5	016	089	125	099	020	006	001	000	000	000	000	000
6	046	000	044	112	076	034	011	003	000	000	000	000
7	036	069	016	010	124	099	051	018	005	001	000	000
8	029	005	063	046	046	115	117	070	028	008	002	000
9	022	005	002	035	012	016	093	125	089	040	012	003
10	039	001	051	022	065	035	001	065	125	107	054	018
11	002	047	007	028	000	047	056	002	037	115	120	069
12	043	005	031	028	052	010	023	065	015	016	099	130
13	013	024	025	009	000	041	028	006	062	033	003	079
14	009	033	004	039	041	011	022	044	000	048	049	000
15	039	000	038	001	008	025	028	006	049	006	030	060
16	013	026	010	025	020	024	009	040	000	044	019	014
17	003	030	007	027	029	005	036	000	041	005	031	033
18	031	002	034	000	000	035	000	036	003	032	016	016
19	030	013	015	022	027	006	028	007	026	014	018	029
20	004	034	001	028	021	012	018	014	019	012	026	007
21	005	019	024	003	000	030	002	028	003	029	003	033
22	030	000	030	008	021	005	027	001	030	000	031	000
23	037	012	009	029	026	008	016	017	009	023	005	026
24	020	034	001	022	004	028	000	025	006	019	012	015

Values in the table are (FCF x 1000)

TABLE 6

Franck-Condon Factors for PbO Large B to X Transitions

$\frac{v''}{v'}$	0	1	2	3	4	5	6	7	8	9	10	11
0	049	160	244	235	165	090	039	014	004	001	000	000
1	126	196	073	001	079	166	168	112	053	019	005	001
2	176	090	006	112	086	003	045	139	159	109	051	018
3	178	009	085	069	003	090	074	002	047	136	148	095
4	150	008	101	000	080	044	009	089	054	000	065	140
5	111	045	049	037	063	005	080	018	028	089	029	008
6	076	075	007	079	005	064	024	028	068	001	056	075
7	049	084	002	067	014	059	007	066	001	059	037	008
8	030	076	019	031	052	012	054	014	040	036	012	067
9	018	061	035	006	064	002	058	006	054	002	060	004
10	011	046	043	000	049	026	022	045	011	043	016	031
11	007	033	043	005	026	046	001	057	004	047	005	049
12	004	023	039	012	009	048	006	035	033	013	041	008
13	003	017	032	016	002	039	020	010	051	001	046	007
14	002	012	026	018	000	026	030	000	044	018	019	037
15	001	009	021	018	001	015	033	002	026	037	001	047
16	001	006	017	017	002	008	029	009	010	043	005	029
17	001	005	013	015	004	003	023	014	002	035	018	008
18	001	004	011	013	005	001	017	017	000	024	029	000
19	000	003	009	012	005	000	012	017	001	013	031	003
20	000	002	007	010	005	000	009	015	003	006	028	010
21	000	002	006	009	005	000	006	013	005	002	022	016
22	000	002	005	007	005	000	004	011	006	000	015	018
23	000	001	004	006	004	000	003	009	006	000	010	018
24	000	001	004	005	004	000	002	007	006	000	007	016

Values in the table are (FCF x 1000)

Values calculated using the Simpson's Rule Approximation

TABLE 6 (cont.)

## Franck-Condon Factors for PbO Large B to X Transitions

$\frac{v''}{v'}$	12	13	14	15	16	17	18	19	20	21	22	23
0	000	000	000	000	000	000	000	000	000	000	000	000
1	000	000	000	000	000	000	000	000	000	000	000	000
2	005	001	000	000	000	000	000	000	000	000	000	000
3	043	015	004	001	000	000	000	000	000	000	000	000
4	133	079	033	011	000	000	000	000	000	000	000	000
5	090	142	115	061	007	001	000	000	000	000	000	000
6	007	030	115	137	042	014	003	001	000	000	000	000
7	077	046	001	065	123	068	026	007	001	000	000	000
8	006	036	077	015	105	139	098	044	014	003	000	000
9	046	043	002	067	000	059	135	125	068	025	006	001
10	039	007	062	010	077	016	018	107	142	096	041	012
11	001	056	006	039	001	066	051	000	064	141	122	063
12	038	017	028	038	059	011	030	075	012	023	118	143
13	039	005	046	001	005	038	041	002	069	043	002	081
14	006	039	006	038	029	033	007	058	007	038	070	006
15	005	035	009	034	043	002	050	002	042	034	008	073
16	029	008	037	003	004	041	009	034	025	013	056	001
17	044	001	036	009	012	029	012	036	006	045	000	051
18	038	018	013	034	036	001	040	000	044	002	030	015
19	022	035	000	038	024	014	019	020	020	022	024	014
20	008	039	005	022	003	034	000	035	001	039	001	041
21	001	032	018	006	003	026	014	014	022	010	030	008
22	000	021	028	000	019	007	032	000	030	002	031	007
23	002	011	030	004	033	000	029	012	013	022	005	031
24	005	005	027	011	035	008	014	029	000	028	003	024

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 7

Franck-Condon Factors for PbO Large C to X Transitions

$\frac{\nu''}{\nu'}$	0	1	2	3	4	5	6	7	8	9	10	11
0	006	037	105	184	223	199	135	071	029	009	002	000
1	024	098	154	105	015	016	106	173	157	094	040	013
2	054	134	089	002	047	104	045	001	072	154	150	091
3	089	118	013	035	084	014	024	091	045	001	074	149
4	117	068	005	076	020	022	072	011	030	087	029	008
5	132	021	042	049	004	063	011	030	061	001	049	077
6	130	000	068	007	043	029	014	054	001	049	040	003
7	117	008	059	004	053	000	049	008	033	034	006	061
8	097	032	030	029	025	021	031	010	042	001	049	008
9	075	056	006	048	001	043	002	039	006	034	017	020
10	056	073	000	044	006	033	009	031	008	034	004	041
11	039	078	013	024	027	009	031	005	032	004	032	007
12	026	075	034	006	039	000	033	004	028	007	027	007
13	017	064	054	000	033	012	015	022	006	028	002	030
14	010	050	067	011	015	028	001	030	002	025	007	021
15	006	036	069	031	002	032	005	018	017	006	024	001
16	003	024	061	051	002	020	019	003	026	001	022	007
17	001	014	049	063	017	006	027	002	018	013	006	022
18	001	008	035	065	038	000	021	012	004	023	001	019
19	000	004	023	057	055	009	008	022	000	018	011	005
20	000	002	013	044	064	028	000	019	008	005	020	001
21	000	001	007	030	062	049	006	008	017	000	017	010
22	000	000	003	018	051	062	023	000	016	006	006	019
23	000	000	001	009	036	063	045	004	007	013	000	016
24	000	000	000	004	022	054	061	021	000	012	004	006

Values in the table are (FCF x 1000)

TABLE 7 (cont.)

Franck-Condon Factors for PbO Large C to X Transitions

$v''$ $v'$	12	13	14	15	16	17	18	19	20	21	22	23
0	000	000	000	000	000	000	000	000	000	000	000	000
1	003	001	000	000	000	000	000	000	000	000	000	000
2	039	013	003	001	000	000	000	000	000	000	000	000
3	137	079	032	010	000	000	000	000	000	000	000	000
4	092	148	121	063	007	001	000	000	000	000	000	000
5	010	025	114	143	046	016	004	001	000	000	000	000
6	070	054	000	055	130	077	032	009	002	000	000	000
7	013	024	078	024	091	140	109	055	020	005	001	000
8	031	050	000	055	003	039	121	131	083	036	012	003
9	040	001	054	021	074	032	004	078	134	111	059	022
10	000	044	012	023	000	048	065	005	031	112	129	086
11	028	018	016	040	051	022	012	071	033	003	071	128
12	030	003	038	000	012	023	049	000	047	063	005	029
13	002	031	005	029	018	037	001	051	018	014	069	030
14	010	020	010	025	035	000	043	007	028	044	000	049
15	028	000	030	000	001	033	009	024	030	004	052	013
16	016	013	012	017	017	018	012	029	003	043	003	034
17	000	025	000	025	027	001	031	000	036	003	032	022
18	007	012	015	006	004	023	005	025	009	021	020	010
19	020	000	022	002	005	019	008	020	007	025	003	034
20	016	007	009	016	021	000	024	000	027	000	030	002
21	004	018	000	018	014	009	011	014	009	017	010	016
22	001	014	008	006	001	020	000	021	002	021	003	024
23	009	003	016	000	005	010	012	005	018	002	021	001
24	017	001	011	008	016	000	017	002	015	006	013	010

Values in the table are (FCF x 1000)

TABLE 8

Franck-Condon Factors for PbO C Prime to X Transitions

$v''$	0	1	2	3	4	5	6	7	8	9	10	11
$v'$												
0	002	014	051	110	171	200	183	134	078	037	014	004
1	010	052	117	138	082	011	012	085	149	151	105	055
2	027	097	122	050	000	052	095	047	000	043	120	144
3	052	119	065	000	053	072	010	021	082	054	001	036
4	080	105	010	033	068	007	029	066	012	019	078	047
5	103	065	003	067	019	018	059	006	029	059	006	028
6	116	025	032	050	001	054	013	021	050	001	040	047
7	117	003	058	014	030	035	005	049	003	034	035	002
8	109	002	059	000	050	003	037	017	017	038	001	046
9	095	017	040	014	036	007	039	001	042	002	035	018
10	079	037	017	036	010	031	012	024	019	015	030	004
11	062	055	002	045	000	039	000	037	000	036	001	034
12	047	066	001	038	011	024	015	019	016	019	014	023
13	035	069	013	020	028	005	032	001	032	000	032	000
14	024	066	029	005	037	001	030	006	022	011	018	013
15	016	057	045	000	032	012	013	022	004	027	001	028
16	010	046	055	006	018	026	001	029	002	023	008	017
17	006	035	058	019	005	032	003	019	015	007	023	001
18	004	025	054	034	000	026	014	005	025	000	022	005
19	002	017	047	045	005	014	025	000	022	009	009	019
20	001	011	038	051	016	003	027	006	010	020	000	021
21	001	007	029	051	029	000	020	017	001	022	005	010
22	000	004	021	046	040	005	009	024	002	013	016	001
23	000	002	014	038	047	016	002	022	010	003	020	003
24	000	001	009	030	047	028	001	014	019	000	015	012

Values in the table are (FCF x 1000)

TABLE 8 (cont.)

Franck-Condon Factors for PbO C Prime to X Transitions

v"	12	13	14	15	16	17	18	19	20	21	22	23
v'												
0	001	000	000	000	000	000	000	000	000	000	000	000
1	023	008	002	000	000	000	000	000	000	000	000	000
2	109	059	025	008	000	000	000	000	000	000	000	000
3	112	136	102	054	007	002	000	000	000	000	000	000
4	000	044	116	130	045	016	005	001	000	000	000	000
5	076	031	002	062	121	075	033	011	003	001	000	000
6	000	044	069	014	087	131	106	056	021	006	001	000
7	052	028	005	062	001	038	113	127	084	038	012	003
8	015	016	055	008	070	026	005	073	128	111	060	023
9	013	044	001	038	000	051	058	004	030	108	127	086
10	041	001	035	025	052	014	016	068	029	003	071	128
11	007	024	025	006	003	032	041	000	048	058	004	032
12	008	031	001	038	030	026	005	051	013	018	067	025
13	032	002	029	009	025	006	042	002	033	038	000	052
14	018	012	022	007	001	036	002	032	022	009	050	007
15	000	029	000	030	029	006	023	020	009	039	000	039
16	012	013	015	014	017	010	025	004	034	000	037	013
17	025	000	026	000	000	029	000	031	002	029	011	018
18	015	012	010	016	019	007	019	010	017	017	011	029
19	001	023	000	023	022	003	022	003	025	002	029	000
20	004	014	011	008	004	021	002	023	001	025	003	025
21	016	002	021	000	003	017	007	014	010	014	011	016
22	020	003	013	011	018	001	021	000	022	000	024	001
23	011	013	002	019	017	005	012	011	007	016	005	019
24	002	018	002	013	004	017	000	019	001	018	004	017

Values in the table are (FCF x 1000)

TABLE 9

Franck-Condon Factors for PbO Large D to X Transitions

$v''$	0	1	2	3	4	5	6	7	8	9	10	11
$v'$												
0	092	260	308	209	093	030	007	001	000	000	000	000
1	173	170	008	080	220	200	103	035	009	002	000	000
2	196	032	064	128	007	071	198	178	089	029	007	001
3	174	002	112	008	079	094	000	096	192	149	068	021
4	133	038	060	027	081	001	102	052	010	130	178	117
5	092	079	008	074	008	068	034	030	104	013	042	151
6	059	097	003	060	013	059	008	079	001	076	071	000
7	036	093	028	021	049	008	056	012	052	042	016	096
8	021	076	056	001	053	005	047	011	053	006	074	004
9	012	057	072	008	028	032	009	046	004	053	010	046
10	006	039	074	030	005	042	002	039	012	036	015	048
11	003	026	066	053	001	029	020	010	038	002	047	001
12	002	016	053	066	016	008	032	000	033	011	025	021
13	001	009	038	068	040	000	025	013	010	032	000	039
14	000	004	024	060	060	011	008	024	000	028	011	017
15	000	002	014	046	068	034	000	019	008	009	029	000
16	000	001	007	030	064	056	009	006	017	000	025	012
17	000	000	003	017	050	068	032	000	013	005	009	027
18	000	000	001	007	032	065	056	011	003	010	000	024
19	000	000	000	002	017	050	068	035	001	007	002	010
20	000	000	000	000	006	031	064	059	016	000	004	001
21	000	000	000	000	001	013	046	068	042	005	002	000
22	000	000	000	001	000	003	023	057	061	024	000	001
23	000	000	000	001	001	000	006	033	060	046	010	000
24	000	000	000	001	002	002	000	011	040	054	028	003

Values in the table are (FCF x 1000)

TABLE 9 (cont.)

Franck-Condon Factors for PbO Large D to X Transitions

V''	12	13	14	15	16	17	18	19	20	21	22	23
V'												
0	000	000	000	000	000	000	000	000	000	000	000	000
1	000	000	000	000	000	000	000	000	000	000	000	000
2	000	000	000	000	000	000	000	000	000	000	000	000
3	005	001	000	000	000	000	000	000	000	000	000	000
4	050	016	004	001	000	000	000	000	000	000	000	000
5	155	091	037	012	001	000	000	000	000	000	000	000
6	078	154	131	071	009	002	001	000	000	000	000	000
7	029	013	104	146	057	023	007	002	000	000	000	000
8	056	079	005	035	134	093	047	019	006	002	000	000
9	046	006	080	049	056	122	122	080	039	016	005	001
10	004	068	011	032	023	007	072	121	110	070	034	014
11	052	011	036	052	056	065	008	017	082	117	100	062
12	028	017	046	001	023	010	067	046	001	028	087	112
13	000	046	000	047	021	055	005	026	066	030	000	036
14	022	015	026	024	046	000	042	038	000	039	060	019
15	032	001	037	001	001	038	023	007	049	020	004	047
16	011	021	008	029	023	025	006	043	006	020	046	009
17	000	024	002	029	032	001	038	005	022	034	000	029
18	013	007	018	005	004	025	013	016	029	000	033	021
19	027	001	017	002	008	022	003	032	000	027	016	005
20	025	015	003	013	028	001	022	007	020	017	003	031
21	013	030	002	010	023	010	014	003	027	001	022	008
22	003	029	019	001	005	028	000	015	005	021	009	004
23	000	017	035	006	000	023	013	007	002	025	002	015
24	000	006	033	024	003	007	030	000	008	007	021	004

Values in the table are (FCF x 1000)

TABLE 10

Franck-Condon Factors for PbO Large E to X Transitions

$\frac{v''}{v'}$	0	1	2	3	4	5	6	7	8	9	10	11
0	000	003	012	035	072	121	164	181	161	117	071	037
1	003	017	052	095	118	098	042	002	020	080	128	132
2	011	051	098	104	055	005	014	065	075	029	000	033
3	033	094	104	043	000	028	062	033	000	032	068	043
4	074	117	054	000	031	054	016	005	045	040	002	020
5	128	090	005	026	051	012	008	042	021	002	037	038
6	179	031	011	054	015	007	038	014	005	036	018	002
7	201	000	043	029	003	034	014	005	031	010	006	033
8	178	045	035	001	034	017	002	029	008	007	029	005
9	117	137	001	009	035	001	020	012	006	022	004	012
10	049	181	035	010	008	030	008	001	025	002	008	021
11	008	125	131	001	000	042	004	008	011	012	010	001
12	000	036	155	048	000	020	040	000	000	029	000	004
13	005	000	075	108	009	005	053	015	000	016	023	001
14	005	011	005	081	039	002	026	048	003	003	038	008
15	001	017	012	011	041	004	004	038	019	001	018	030

Values in the table are (FCF x 1000)

TABLE 10 (cont.)

Franck-Condon Factors for PbO Large E to X Transitions

$\frac{v''}{v'}$	12	13	14	15	16	17	18	19	20	21	22	23
0	017	007	002	001	000	000	000	000	000	000	000	000
1	102	062	031	013	001	000	000	000	000	000	000	000
2	092	123	108	072	017	007	002	001	000	000	000	000
3	003	017	072	110	075	043	021	009	003	001	000	000
4	060	045	005	011	098	100	076	046	024	011	004	002
5	003	017	056	043	008	051	089	095	075	049	027	013
6	035	034	002	018	040	006	006	044	080	089	075	052
7	013	003	035	029	019	049	037	006	004	036	070	084
8	009	031	008	006	024	000	018	045	035	007	002	027
9	023	002	015	027	010	033	020	000	016	041	035	010
10	000	014	019	000	024	001	010	032	018	000	013	035
11	018	009	000	021	000	021	017	001	011	026	019	001
12	018	003	009	011	013	011	003	015	020	001	005	026
13	002	026	000	000	001	001	025	003	000	021	011	006
14	000	023	014	001	015	003	010	011	005	016	003	003
15	001	006	033	002	030	002	000	028	000	001	025	001

Values in the table are (FCF x 1000)

TABLE 11

Franck-Condon Factors for PbO A to Small A Transitions

v'' v'	0	1	2	3	4	5	6	7	8	9	10	11
0	918	070	010	002	000	000	000	000	000	000	000	000
1	082	765	120	026	006	001	000	000	000	000	000	000
2	000	164	623	154	043	012	003	001	000	000	000	000
3	000	000	244	493	174	060	020	006	002	000	000	000
4	000	000	002	320	378	182	075	029	010	003	001	000
5	000	000	000	004	390	277	180	086	038	015	005	002
6	000	000	000	000	009	451	193	171	094	048	021	008
7	000	000	000	000	001	016	502	125	157	098	056	027
8	000	000	000	000	000	001	026	541	071	140	099	063
9	000	000	000	000	000	000	001	041	567	033	122	097
10	000	000	000	000	000	000	000	000	061	576	010	103
11	000	000	000	000	000	000	000	000	000	087	567	000
12	000	000	000	000	000	000	000	000	000	000	118	542
13	000	000	000	000	000	000	000	000	000	001	000	155
14	000	000	000	000	000	000	000	000	000	000	001	002
15	000	000	000	000	000	000	000	000	000	000	000	001
16	000	000	000	000	000	000	000	000	000	000	000	000
17	000	000	000	000	000	000	000	000	000	000	000	000
18	000	000	000	000	000	000	000	000	000	000	000	000
19	000	000	000	000	000	000	000	000	000	000	000	000
20	000	000	000	000	000	000	000	000	000	000	000	000
21	000	000	000	000	000	000	000	000	000	000	000	000
22	000	000	000	000	000	000	000	000	000	000	000	000
23	000	000	000	000	000	000	000	000	000	000	000	000
24	000	000	000	000	000	000	000	000	000	000	000	000

Values in the table are (FCF x 1000)

TABLE 11 (cont.)

Franck-Condon Factors for PbO A to Small A Transitions

v''	12	13	14	15	16	17	18	19	20	21	22	23
v'												
0	000	000	000	000	000	000	000	000	000	000	000	000
1	000	000	000	000	000	000	000	000	000	000	000	000
2	000	000	000	000	000	000	000	000	000	000	000	000
3	000	000	000	000	000	000	000	000	000	000	000	000
4	000	000	000	000	000	000	000	000	000	000	000	000
5	001	000	000	000	000	000	000	000	000	000	000	000
6	003	001	000	000	000	000	000	000	000	000	000	000
7	012	005	002	001	000	000	000	000	000	000	000	000
8	033	016	007	002	000	000	000	000	000	000	000	000
9	068	039	020	009	001	000	000	000	000	000	000	000
10	093	071	045	024	004	002	001	000	000	000	000	000
11	085	088	073	050	013	006	002	001	000	000	000	000
12	004	067	082	073	032	016	007	003	001	000	000	000
13	501	018	051	076	057	036	019	009	004	001	000	000
14	194	447	042	035	070	059	040	023	011	005	002	001
15	004	235	382	073	061	067	060	044	026	014	006	002
16	002	009	274	311	010	054	063	061	047	030	016	008
17	000	003	017	309	148	003	045	060	060	050	033	019
18	000	001	005	028	166	184	000	037	056	059	052	037
19	000	000	001	008	353	101	214	003	029	051	057	053
20	000	000	000	002	061	356	048	234	014	020	047	055
21	000	000	000	000	018	081	343	014	240	031	012	043
22	000	000	000	000	005	026	104	314	000	230	055	005
23	000	000	000	000	000	008	037	125	270	008	204	084
24	000	000	000	000	000	001	012	051	143	215	035	164

Values in the table are (FCF x 1000)

TABLE 12

Franck-Condon Factors for PbO D to Small A Transitions

$v''$	0	1	2	3	4	5	6	7	8	9	10	11
$v'$												
0	526	330	114	026	004	000	000	000	000	000	000	000
1	358	081	294	190	063	012	001	000	000	000	000	000
2	102	358	000	194	218	099	025	003	000	000	000	000
3	013	195	276	017	112	213	127	040	007	000	000	000
4	001	034	258	201	045	058	191	145	055	011	001	000
5	000	002	056	297	150	064	027	163	153	069	017	002
6	000	000	002	072	325	122	071	012	136	154	080	023
7	000	000	000	002	082	348	113	068	004	113	150	087
8	000	000	000	000	001	082	369	118	060	001	096	142
9	000	000	000	000	001	000	073	388	137	047	000	084
10	000	000	000	000	000	001	001	055	399	170	031	000
11	000	000	000	000	000	000	002	005	032	396	217	016
12	000	000	000	000	000	000	000	002	014	011	369	275
13	000	000	000	000	000	000	000	000	001	025	000	313
14	000	000	000	000	000	000	000	000	001	000	036	010
15	000	000	000	000	000	000	000	000	000	002	000	039
16	000	000	000	000	000	000	000	000	000	000	002	005
17	000	000	000	000	000	000	000	000	000	000	000	002
18	000	000	000	000	000	000	000	000	000	000	000	002
19	000	000	000	000	000	000	000	000	000	000	000	000
20	000	000	000	000	000	000	000	000	000	000	000	000
21	000	000	000	000	000	000	000	000	000	000	000	000
22	000	000	000	000	000	000	000	000	000	000	000	000
23	000	000	000	000	000	000	000	000	000	000	000	000
24	000	000	000	000	000	000	000	000	000	000	000	000

Values in the table are (FCF x 1000)

TABLE 12 (cont.)

Franck-Condon Factors for PbO D to Small A Transitions

V''	12	13	14	15	16	17	18	19	20	21	22	23
V'												
0	000	000	000	000	000	000	000	000	000	000	000	000
1	000	000	000	000	000	000	000	000	000	000	000	000
2	000	000	000	000	000	000	000	000	000	000	000	000
3	000	000	000	000	000	000	000	000	000	000	000	000
4	000	000	000	000	000	000	000	000	000	000	000	000
5	000	000	000	000	000	000	000	000	000	000	000	000
6	003	000	000	000	000	000	000	000	000	000	000	000
7	028	005	000	000	000	000	000	000	000	000	000	000
8	092	032	006	000	000	000	000	000	000	000	000	000
9	134	093	035	007	000	000	000	000	000	000	000	000
10	078	126	093	037	001	000	000	000	000	000	000	000
11	000	076	117	091	009	001	000	000	000	000	000	000
12	004	001	078	106	038	010	001	000	000	000	000	000
13	337	000	004	085	088	038	012	002	000	000	000	000
14	227	387	009	010	076	089	037	014	003	001	000	000
15	046	125	406	030	121	056	092	035	017	004	001	000
16	031	104	037	372	044	154	033	101	029	020	005	002
17	017	012	159	000	068	068	198	013	118	021	025	005
18	000	032	000	174	156	055	083	243	001	147	011	035
19	003	001	039	018	128	049	021	072	264	002	188	002
20	001	003	011	027	043	192	003	000	035	234	012	232
21	000	002	001	029	125	000	169	004	027	002	144	015
22	000	000	004	001	006	118	036	079	005	082	012	042
23	000	000	001	004	028	054	049	094	011	001	091	047
24	000	000	000	005	036	002	105	001	082	000	042	036

Values in the table are (FCF x 1000)

### Molecular Bromine

Three isotopic forms of molecular Bromine were studied, the (79,79) isotope, the (81,81) isotope, and the (79,81) mixture of both isotopic states. Five electronic states were calculated for the first isotope (A', B, D', E, X) and two states each (B, X) for the (81,81) isotope and the mixed isotope. The data used to calculate the bromine potentials is given in Table 13. The number next to the state name is the bibliographic entry for the journal article from which the molecular constants were drawn. The dissociation energy for the B and X states of bromine are difficult to calculate and not widely available in the open literature. Because of this, three spectroscopic dissociation energies (79:B, 81:B, 79,81:X) had to be calculated from the chemical dissociation energies which were published in the article by Barrow and others (2). The formula used to make the conversion was:

$$D_e = D_o + 1/2\omega_e - 1/4\omega_e X_e + 1/8\omega_e Y_e \quad (22)$$

where  $D_e$  is the desired spectroscopic dissociation energy,  $D_o$  is the chemical dissociation energy and  $\omega_e$ ,  $\omega_e X_e$ ,  $\omega_e Y_e$  are the molecular constants described in Section II. Three dissociation energies (79:X, 81:X, 79,81:B) had to be extrapolated from available data because no specific energy data was available. The method of extrapolation is described in Appendix C. The remaining three dissociation energies were available in the literature.

TABLE 13  
Data for Molecular Bromine  
Part I. (79,79)

STATE	A' (26)	B (2)	D' (26)	E (3)	X (2)
$T_e$	13220	15902.47	48930	49779.06	0
$\omega_e$	165.172	167.6066	150.863	150.465	325.3213
$\omega_e x_e$	2.504	1.63608	0.3842	0.3829	1.07742
$B_e$	0.059439	0.059589	0.042515	0.041720	0.082107
$\alpha_e$	5.604E-4	4.891E-4	1.507E-4	1.41E-4	3.187E-4
$D_e$	3.079E-8	3.013E-8	1.351E-8	1.28E-8	2.092E-8
$R_e$	---	2.6776	---	3.20	2.28107
Dis. En.	2835	* 19663.16	35550	34704	** 16055.981

All values in inverse cm except  $R_e$  which is in Angstroms  
Numbers in parentheses represent bibliographic entry of  
source article

\* See Equation 22

\*\* Extrapolated from available data (see Appendix C)

TABLE 13  
Data for Molecular Bromine  
Part II. (79,81) and (81,81)

STATE	(79,81)B (2)	(79,81)X (2)	(81,81)B (2)	(81,81)X (2)
$T_e$	15902.47	0	15902.47	0
$\omega_e$	166.5688	323.3069	165.5244	321.29
$\omega_e x_e$	1.6159	1.0641	1.5957	1.064
$B_e$	.058853	.081093	.058118	.080088
$\alpha_e$	4.8007 E-4	3.1285 E-4	4.7109 E-4	3.19 E-4
$D_e$	2.939 E-8	2.041 E-8	2.866 E-8	1.99 E-8
$R_e$	2.6776	2.28107	2.6776	2.28107
Dis. **		*	*	**
En.	19663.7	16056.988	19664.184	16057.996

All values in inverse cm except  $R_e$  which is in Angstroms  
Numbers in parentheses represent bibliographic entry of  
source article

\* See Equation 22

\*\* Extrapolated from available data (see Appendix C)

The Franck-Condon Factors for molecular bromine are listed in Tables 14 through 19. Literature values of the Franck-Condon Factors are available for two transitions, E to B and D' to A'. The calculated and literature values of the Franck-Condon Factors for the D' to A' transition are shown in Table 20. The entries are in the following order: literature value, calculated value, and the absolute difference between the two values. Although the Franck-Condon Factors differ between the calculated and literature values, for the most part the agreement between both sets of numbers is good. The most noticeable derivation occurs at the values of the higher quantum numbers, where the IPA routine would have the most effect. The potentials for the literature values were calculated with only the RKR approximation and thus do not have the added accuracy the IPA adds to the higher energy region of the curve. It is believed that the values presented in this paper are more accurate in this region because of the addition of the IPA. The IPA increases the accuracy of the potential energy values by repeated comparisons between the calculated and spectroscopic energy values and associated corrections to the potential energy function. The most important thing to note from the comparison between the calculated and literature factors however, is that the Condon Parabola shows good agreement between the two sets of Franck-Condon Factors. Both sets of factors therefore predict the same transitions to be most probable even though the factors themselves differ

TABLE 14

Franck-Condon Factors for Br<sub>2</sub> (79) Lg B to X Transitions

$\frac{v''}{v'}$	0	1	2	3	4	5	6	7
0	000	000	000	000	000	000	000	001
1	000	000	000	000	000	000	001	004
2	000	000	000	000	000	002	005	012
3	000	000	000	000	001	005	012	027
4	000	000	000	001	003	010	024	043
5	000	000	000	002	007	019	037	052
6	000	000	001	004	014	029	046	049
7	000	000	002	008	021	038	047	035
8	000	001	004	013	019	043	040	016
9	000	001	007	019	036	042	026	003
10	000	002	010	026	041	036	012	000
11	000	004	015	033	041	025	002	006
12	001	006	021	039	037	013	000	016
13	001	009	028	041	028	004	005	022
14	002	013	034	040	018	000	013	022
15	003	017	038	036	009	002	020	015

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 14 (cont.)

Franck-Condon Factors for Br<sub>2</sub> (79) Lg B to X Transitions

$v''$ $v'$	8	9	10	11	12	13	14	15
0	002	004	009	017	029	045	064	084
1	010	020	035	051	065	073	071	056
2	026	044	059	064	055	036	013	000
3	046	060	057	038	014	001	006	026
4	057	052	029	006	001	016	034	036
5	050	027	004	003	021	034	026	006
6	029	005	003	022	033	020	002	004
7	009	001	019	032	018	001	006	024
8	000	013	030	020	002	006	023	021
9	005	025	024	004	004	021	020	003
10	017	027	009	001	017	021	005	003
11	024	017	000	011	022	008	001	015
12	023	005	004	020	013	000	011	019
13	014	000	014	018	002	005	018	008
14	004	004	019	008	001	015	013	000
15	000	013	016	001	009	016	003	005

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 15

Franck-Condon Factors for Br<sub>2</sub> (79) A' to X Transitions

$\frac{v''}{v'}$	0	1	2	3	4	5	6	7
0	000	000	000	000	000	000	000	001
1	000	000	000	000	000	000	001	003
2	000	000	000	000	000	001	004	011
3	000	000	000	000	001	004	011	024
4	000	000	000	001	003	010	022	039
5	000	000	001	002	007	018	034	049
6	000	000	001	005	014	029	044	048
7	000	000	003	009	022	038	046	035
8	000	001	005	016	031	043	039	017
9	000	002	009	024	039	042	025	003
10	001	004	015	032	042	033	010	000
11	001	008	023	040	040	020	001	007
12	002	013	032	044	032	007	001	017
13	004	020	041	042	019	001	008	021
14	007	030	047	035	007	002	017	017
15	012	039	048	023	001	009	020	008

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 15 (cont.)

Franck-Condon Factors for Br<sub>2</sub> (79) A' to X Transitions

v'' v'	8	9	10	11	12	13	14	15
0	001	004	008	015	026	040	059	078
1	008	017	031	046	061	070	071	060
2	023	039	055	062	057	040	019	003
3	041	056	057	042	019	003	002	018
4	053	053	033	010	000	009	027	036
5	050	031	007	001	014	030	029	012
6	032	008	001	016	030	024	006	001
7	011	000	014	028	021	004	002	017
8	000	009	026	022	004	002	016	022
9	004	022	024	006	001	015	021	008
10	015	025	010	000	012	020	009	000
11	023	016	001	008	019	011	000	009
12	020	004	003	017	014	001	006	016
13	011	000	012	016	003	003	014	010
14	002	006	017	007	000	011	012	001
15	001	013	012	000	007	013	004	002

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 16

Franck-Condon Factors for Br<sub>2</sub> (79) D' to A' Transitions

v''	0	1	2	3	4	5	6	7
v'								
0	000	000	000	000	000	002	010	038
1	000	000	000	000	002	010	037	088
2	000	000	000	001	006	025	066	100
3	000	000	000	003	014	044	080	068
4	000	000	001	006	025	060	072	025
5	000	000	002	011	038	067	047	001
6	000	000	004	019	050	062	019	005
7	000	001	007	028	058	046	002	023
8	000	001	011	037	058	026	002	035
9	000	002	015	044	050	009	012	032

Values in table are (FCF x 1000)

Values calculated with the Simpson's Rule Approximation

TABLE 16 (cont.)

Franck-Condon Factors for Br<sub>2</sub> (79) D' to A' Transitions

$v''$	8	9	10	11	12	13	14	15
$v'$								
0	103	198	265	233	120	028	001	001
1	130	091	006	057	234	249	086	002
2	067	003	041	080	003	114	309	160
3	009	021	064	008	033	038	030	304
4	004	050	020	013	049	000	033	004
5	028	037	000	040	007	030	024	007
6	041	009	019	026	005	031	002	045
7	030	001	033	002	026	006	022	003
8	010	014	021	005	024	003	023	004
9	000	027	004	021	006	019	003	021

Values in the table are (FCF x 1000)

Values calculated with the Simpson's Rule Approximation

TABLE 17

Franck-Condon Factors for Br<sub>2</sub> (79) E to B Transitions

$v''$ $v'$	0	1	2	3	4	5	6	7	8	9
0	000	000	000	000	000	000	001	004	014	042
1	000	000	000	000	000	001	004	017	046	091
2	000	000	000	000	001	003	013	039	077	094
3	000	000	000	000	002	008	028	061	081	050
4	000	000	000	001	004	017	045	072	056	008
5	000	000	000	002	009	029	058	062	021	002
6	000	000	000	003	015	040	061	039	001	022
7	000	000	001	006	023	049	053	015	004	037
8	000	000	002	010	031	052	037	002	019	032
9	000	000	003	015	038	049	019	001	030	015
10	000	001	005	021	044	041	006	011	030	002
11	000	001	008	027	047	029	000	022	020	001
12	000	002	011	034	045	016	003	028	007	011
13	000	003	016	039	040	006	011	025	000	020
14	000	004	020	042	030	000	019	017	002	022
15	000	006	025	043	020	001	025	007	010	015
16	001	008	029	040	010	006	024	001	017	006
17	001	010	033	035	004	013	019	001	020	000
18	001	013	036	029	000	019	012	005	016	001
19	002	016	037	021	001	022	005	011	010	007
20	003	019	037	014	004	022	001	016	003	013
21	004	023	036	008	008	019	000	018	000	015
22	005	026	034	003	013	014	003	015	001	014
23	006	028	030	001	017	008	008	010	005	009
24	007	031	025	000	020	003	012	005	010	004

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 17 (cont.)

Franck-Condon Factors for Br<sub>2</sub> (79) E to B Transitions

$v''$ $v'$	10	11	12	13	14	15	16	17	18	19
0	095	166	219	215	151	071	002	000	000	000
1	120	087	017	013	121	217	074	011	000	001
2	054	002	030	085	041	005	242	150	028	000
3	002	025	064	019	012	072	037	229	226	052
4	013	053	020	008	054	013	055	001	176	284
5	041	030	001	041	017	012	000	042	006	119
6	039	002	025	028	002	039	031	021	013	015
7	016	007	034	002	026	015	028	004	039	000
8	001	025	016	007	028	000	001	029	002	035
9	005	028	001	024	007	016	012	016	011	016
10	019	015	006	023	001	024	024	000	025	000
11	025	002	019	007	013	011	011	011	009	015
12	019	002	021	000	021	000	000	020	000	018
13	007	012	012	007	013	006	008	009	012	004
14	000	019	002	017	002	016	017	000	016	002
15	003	017	001	016	001	015	012	006	007	012
16	011	008	009	008	009	005	002	014	000	014
17	017	001	015	001	015	000	001	011	005	005
18	016	001	015	001	012	003	008	003	012	000
19	010	006	008	007	005	010	012	000	010	005
20	004	012	002	013	000	013	010	005	003	010
21	000	014	000	012	002	009	003	010	000	009
22	001	011	003	008	007	003	000	010	003	003
23	006	006	009	002	011	000	003	005	008	000
24	011	001	012	000	011	002	008	000	009	002

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 17 (cont.)

Franck-Condon Factors for Br<sub>2</sub> (79) E to B Transitions

$v''$ $v'$	20	21	22	23	24	25	26	27	28	29
0	000	000	000	000	000	000	000	000	000	000
1	000	000	000	000	000	000	000	000	000	000
2	002	000	000	000	000	000	000	000	000	000
3	000	006	001	000	000	000	000	000	000	000
4	080	001	014	001	001	000	000	000	000	000
5	321	105	004	027	000	004	000	001	000	000
6	076	336	121	011	044	000	009	000	002	000
7	013	049	332	123	026	062	002	016	001	003
8	010	005	035	310	108	053	073	011	022	006
9	018	032	000	030	270	077	092	070	033	021
10	022	005	053	008	029	213	039	135	047	072
11	005	016	000	069	032	030	143	009	163	015
12	003	015	006	000	081	066	027	071	000	153
13	016	000	021	000	000	091	100	018	017	010
14	012	007	004	021	003	000	100	120	005	000
15	001	015	001	008	017	015	003	103	112	001
16	003	007	011	001	009	014	036	012	094	076
17	011	000	012	005	005	006	012	065	024	067
18	011	004	004	011	001	011	001	014	096	034
19	003	011	000	008	006	000	018	000	019	120
20	000	009	006	001	010	002	001	024	008	027
21	004	002	010	001	005	009	000	001	032	025
22	009	000	007	006	000	007	006	002	000	042
23	008	004	001	009	002	002	007	003	007	000
24	003	008	000	005	007	000	005	005	002	018

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 18

Franck-Condon Factors for Br<sub>2</sub> (81) B to X Transitions

$\frac{v''}{v'}$	0	1	2	3	4	5	6	7
0	000	000	000	000	000	000	000	001
1	000	000	000	000	000	000	001	003
2	000	000	000	000	000	001	004	011
3	000	000	000	000	001	004	011	025
4	000	000	000	001	003	009	022	041
5	000	000	000	002	007	018	035	051
6	000	000	001	004	012	027	044	050
7	000	000	002	007	019	036	047	037
8	000	001	003	012	027	042	041	019
9	000	001	006	018	035	042	029	005
10	000	002	009	025	040	037	015	000
11	000	003	014	032	041	027	004	004
12	001	006	020	038	038	015	000	014
13	001	008	026	041	031	005	003	021
14	002	012	032	041	021	000	011	022
15	003	016	037	037	011	001	018	017

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 18 (cont.)

Franck-Condon Factors for Br<sub>2</sub> (81) B to X Transitions

$\frac{v''}{v'}$	8	9	10	11	12	13	14	15
0	002	004	009	016	028	044	063	084
1	009	018	033	049	064	074	072	057
2	024	042	058	065	057	038	015	001
3	044	059	059	042	017	001	005	024
4	056	054	033	008	000	014	033	037
5	051	030	006	002	019	034	028	008
6	032	007	002	020	033	022	003	004
7	011	000	017	032	020	002	005	023
8	000	010	029	022	003	005	022	022
9	003	023	026	006	002	020	0021	004
10	014	027	011	000	015	022	006	002
11	023	019	001	009	022	010	000	014
12	024	007	002	019	015	000	009	019
13	016	000	012	019	003	004	018	009
14	006	003	019	010	000	014	014	000
15	000	011	017	001	007	017	004	004

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 19

Franck-Condon Factors for Br<sub>2</sub> (79,81) B to X Transitions

$v''$ $v'$	0	1	2	3	4	5	6	7
0	000	000	000	000	000	000	000	001
1	000	000	000	000	000	000	001	004
2	000	000	000	000	000	001	004	012
3	000	000	000	000	001	004	012	026
4	000	000	000	001	003	010	023	042
5	000	000	000	002	007	018	036	051
6	000	000	001	004	013	028	045	049
7	000	000	002	008	020	037	047	036
8	000	001	004	012	028	042	040	018
9	000	001	006	018	035	042	028	004
10	000	002	010	025	040	036	014	000
11	000	004	015	032	041	026	003	005
12	001	006	021	038	038	014	000	015
13	001	009	027	041	030	005	004	022
14	002	012	033	041	020	000	012	022
15	003	017	038	036	010	002	019	016

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 19 (cont.)

Franck-Condon Factors for Br<sub>2</sub> (79,81) B to X Transitions

$\frac{v''}{v'}$	8	9	10	11	12	13	14	15
0	002	004	009	016	028	043	062	082
1	009	019	033	049	063	072	071	057
2	025	042	058	064	056	028	015	001
3	044	059	058	040	016	001	004	023
4	056	054	032	007	000	014	032	036
5	051	029	005	002	019	034	027	008
6	031	006	002	021	033	022	003	003
7	010	001	018	032	020	002	005	023
8	000	011	029	022	002	005	022	022
9	004	024	025	005	003	020	021	005
10	015	027	011	000	016	022	006	002
11	024	018	001	010	022	010	000	014
12	024	006	003	019	015	000	009	019
13	015	000	012	019	003	004	018	009
14	005	004	019	010	000	014	014	000
15	000	012	016	001	007	017	004	003

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 20

Franck-Condon Factors for Br<sub>2</sub>, D' to A' Transitions  
Comparison of Literature and Calculated Values  
(FCF x 1000)

v"	0	1	2	3	4	5	6	7
v'	-	-	0	0	0	2	12	44
0	0	0	0	0	0	2	10	38
	-	-	0	0	0	0	2	6
	-	-	0	0	2	11	39	94
1	0	0	0	0	2	10	37	88
	-	-	0	0	0	1	2	6
	-	-	0	1	6	26	69	103
2	0	0	0	1	6	25	66	100
	-	-	0	0	0	1	3	3
	-	-	0	3	14	46	84	67
3	0	0	0	3	14	44	80	68
	-	-	0	0	0	2	4	1
	-	-	0	6	26	63	73	22
4	0	0	1	6	25	60	72	25
	-	-	1	0	1	3	1	3
	-	-	2	12	39	69	46	0
5	0	0	2	11	38	67	47	1
	-	-	0	1	1	2	1	1

Order of entries: literature Franck-Condon Factor  
calculated Franck-Condon Factor  
absolute difference of the two values

TABLE 20 (cont.)

Franck-Condon Factors for  $\text{Br}_2$ , D' to A' Transitions  
Comparison of Literature and Calculated Values  
(FCF x 1000)

$v''$	8	9	10	11	12	13	14	15
$v'$	118	225	286	221	83	7	1	0
0	103	198	265	233	120	28	1	1
	15	27	21	12	37	21	0	1
	133	79	0	117	302	196	17	6
1	130	91	6	57	234	249	86	2
	3	12	6	60	68	53	69	4
	61	0	58	64	9	266	285	17
2	67	3	41	80	3	114	309	160
	6	3	17	16	6	152	24	143
	5	31	60	0	53	2	217	330
3	9	21	64	8	33	38	30	304
	4	10	4	8	20	36	187	26
	8	55	10	31	33	10	6	196
4	4	50	20	13	49	0	33	4
	4	5	10	18	16	10	27	192
	34	31	5	42	0	49	1	1
5	28	37	0	40	7	30	24	7
	6	6	5	2	7	19	23	6

Order of entries: literature Franck-Condon Factor  
calculated Franck-Condon Factor  
absolute difference of the two values

in value. The coincidence of the parabolas indicates that the calculation of potential energy curves by the RKR method is adequate for most purposes. In Table 20, the parabola is represented by lines connecting maximum values within one set. Thus, even though the calculated values differ from the ones published in the literature, the transitions displaying maximum probabilities have not been shifted but show good agreement with the published maximums. Similiar results are seen when the two sets of Franck-Condon Factors for the E to B transition are compared and the Condon Parabolas drawn in. Each of the three B to X transitions also exhibit clear Condon Parabolas.

Further computer runs were made to test the sensitivity of the wavefunction values to the number of points at which they are evaluated. The potentials and waveunctions for the E to B transition were recalculated using 631 points to evaluate the wavefunction. Program FCFACT was rerun using these values. No substantial change in the values of the Franck-Condon Factors was noted. This observation indicates that the initial use of 301 points insures accuracy in the calculation of the wavefunctions.

#### Bromine Chloride

Two isotopic configurations of BrCl were studied,  $^{81}\text{Br}^{35}\text{Cl}$  and  $^{79}\text{Br}^{35}\text{Cl}$ . The Franck-Condon Factors for the B to X transitions were calculated for each molecule of the pair. The molecular constants were derived from two sources, an

article by J. A. Coxon published in the Journal of Molecular Spectroscopy (7) and a thesis prosectus written by Glen Perram (19). Because of the lack of published data, the dissociation energy must once again be extrapolated from available data (see Appendix C). The data for both molecules of BrCl is listed in Table 21. The potentials and values of the wavefunctions were evaluated at 301 points on each vibrational level. Here again, the number of points at which the wavefunctions were evaluated was increased to test its effect on the values. The number of points was increased to 901, almost triple the original values, but the change in the Franck-Condon Factors was very small. The Franck-Condon Factors for both transitions studied are tabulated in Tables 22 and 23.

When the calculated results were compared to the literature values of the Franck-Condon Factors for BrCl, there was poor agreement between the two sets of data. Table 24 contains a comparison between literature and calculated values similiar to those described earlier. As can be seen from this table, not only is the comparison between values poor but the maximum value lines do not correspond. These lines should be the Condon Parabola but that feature is poorly formed in these two sets of Franck-Condon Factors. The calculations for the constants for the B state in the literature (7) include a perturbation term which was not included as part of the data for the calculations of the B state potential and wavefunctions for this thesis. It was

TABLE 21  
Data for Bromine Chloride

STATE (79,35)B (7) (79,35)X (7) (81,35)B (7) (81,35)X (7)

$T_e$	16879.9	0	16881.2	0
$\omega_e$	222.68	444.276	221.87	442.589
$\omega_e x_e$	2.884	1.843	2.848	1.879
$B_e$	.107704	.1524695	.106919	.1513093
$D_e$	1.0078 E-7	7.183 E-8	9.9318 E-8	7.074 E-8
$R_e$	2.5415	2.138	2.5411	2.138
Dis.		**		**
En.	18936.3	18211	18945.2	18211.844

All values in inverse cm except  $R_e$  which is in Angstroms  
Numbers in parentheses represent bibliographic entry of  
source article

\*\* Extrapolated from available data (see Appendix C)

TABLE 22

Franck-Condon Factors for BrCl (79) B to X Transitions

$v''$ $v'$	0	1	2	3	4	5	6	7
0	000	000	000	000	000	000	001	001
1	000	000	000	000	001	002	005	010
2	000	000	001	002	005	011	020	034
3	000	001	003	008	017	030	046	059
4	000	003	009	022	039	055	062	054
5	002	009	024	045	060	061	043	018
6	006	022	047	064	060	035	009	000
7	014	044	067	062	032	005	003	021
8	031	069	071	036	004	005	025	032

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 23

Franck-Condon Factors for BrCl (81) B to X Transitions

$\begin{smallmatrix} v'' \\ v' \end{smallmatrix}$	0	1	2	3	4	5	6	7
0	000	000	000	000	000	000	001	001
1	000	000	000	000	001	002	005	010
2	000	000	001	002	005	010	020	033
3	000	001	003	007	016	030	046	059
4	000	003	009	021	038	054	062	054
5	002	009	024	044	060	061	044	018
6	005	022	046	064	060	036	009	000
7	014	043	067	063	033	005	002	021
8	030	068	071	037	004	004	025	032

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 24

Franck-Condon Factors for BrCl, B to X Transitions  
Comparison of Literature and Calculated Values  
(FCF x 1000)

v''	0	1	2	3	4	5	6	7
v'	0	0	0	0	0	0	1	<u>3</u>
0	0	0	0	0	0	0	1	1
	0	0	0	0	0	0	0	2
1	0	0	0	0	1	2	6	<u>15</u>
	0	0	0	0	1	2	5	<u>10</u>
	0	0	0	0	0	0	1	5
2	0	0	0	0	2	6	16	<u>33</u>
	0	0	1	2	5	11	20	<u>34</u>
	0	0	1	2	3	5	4	1
3	0	0	0	1	5	14	30	<u>50</u>
	0	1	3	8	17	30	46	<u>59</u>
	0	1	3	7	12	16	16	9
4	0	0	1	3	10	24	42	<u>53</u>
	0	3	9	22	39	55	<u>62</u>	<u>54</u>
	0	3	8	19	29	31	20	1
5	0	0	1	5	15	32	<u>46</u>	<u>44</u>
	2	9	24	45	60	<u>61</u>	43	18
	2	9	23	40	45	29	3	26
6	0	0	2	8	20	36	<u>42</u>	27
	6	22	47	<u>64</u>	60	35	9	0
	6	22	45	56	40	1	33	27
7	0	0	3	10	24	<u>36</u>	32	12
	14	44	<u>67</u>	62	32	5	3	21
	14	44	64	52	8	31	29	9
8	0	1	3	11	24	<u>31</u>	20	3
	31	69	<u>71</u>	36	4	5	25	32
	31	68	68	25	20	26	5	29

Order of entries: literature Franck-Condon Factor  
calculated Franck-Condon Factor  
absolute difference of the two values

not possible to avoid the effects of this perturbation term with the present form of the potential modelling program. Because of this, further calculations of Franck-Condon Factors for BrCl were discontinued.

#### Bromine Monofluoride

BrF is one of the least studied molecules of the interhalogens. Because of this, the amount of data available in the literature is small. Only one transition, the B to X has been studied. Values for the molecular constants have been reported for the B state with a natural mixture of the  $^{79}\text{Br}$  and  $^{81}\text{Br}$  isotopes. The lower state constants have been reported for the isotopically pure  $^{79}\text{Br}-^{19}\text{F}$ . These constants were used in the present study to calculate the potentials for the B and X states and Franck-Condon Factors for the B to X transition. The values for these constants are shown in Table 25. The wavefunction was evaluated at 301 points between the minimum and maximum internuclear distances. The Frank-Condon Factors for the BrF B to X transition are included as Table 26. No literature values for the Franck-Condon Factors were uncovered during the literature search conducted for this thesis.

#### Iodine Chloride

Although many states of iodine chloride are known, few of them have been characterized in depth. The literature search for this thesis produced molecular constants for five

TABLE 25  
Data for Bromine Monofluoride

STATE	B (19)	X (9)
$T_e$	18650	0
$\omega_e$	365	669.823
$\omega_e x_e$	6	3.753
$B_e$	0.25659	0.3558193
$\alpha_e$	----	2.5826 E-3
$R_e$	2.0689	1.758995
Dissociation Energy	5000	20622

All values in inverse cm except  $R_e$  which is in Angstroms

Numbers in parentheses represent bibliographic entry of  
source article for the number

TABLE 26

Franck-Condon Factors for BrF Large B to X Transitions

$v''$ $v'$	0	1	2	3	4	5	6	7
0	000	000	001	002	004	007	013	020
1	000	002	006	013	023	035	049	059
2	003	010	024	041	056	065	064	052
3	011	032	056	070	067	049	025	006
4	032	068	081	064	032	007	000	011
5	074	097	066	021	000	009	027	034
6	129	088	021	000	020	036	029	010
7	176	040	000	027	040	021	002	004
8	191	002	028	044	017	000	012	025

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 26 (cont.)

Franck-Condon Factors for BrF Large B to X Transitions

$v''$	8	9	10	11	12	13	14	15
$v'$								
0	030	041	052	064	074	081	085	085
1	066	065	058	045	029	014	004	000
2	034	016	003	000	007	020	033	040
3	000	007	021	033	035	027	013	003
4	027	034	027	013	002	001	010	022
5	024	008	000	005	018	025	022	010
6	000	007	020	024	016	004	000	007
7	018	024	015	003	001	010	019	018
8	019	005	000	010	019	016	005	000

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

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CALCULATION OF FRANCK-CONDON FACTORS FOR DIATOMIC  
MOLECULES(U) AIR FORCE INST OF TECH WRIGHT-PATTERSON  
AFB OH SCHOOL OF ENGINEERING L D BRASURE MAR 85

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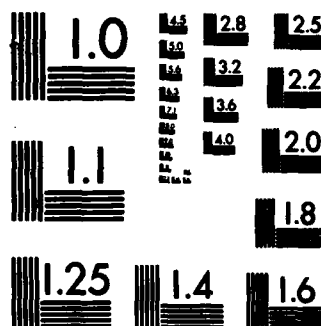
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well-known states of ICl split between two isotopic configurations. Three electronic states, A, B, and X, were modelled for  $I^{35}Cl$  and two states, B and X, were modelled for  $I^{37}Cl$ . The molecular constants used to calculate the potential energy curves are shown in Table 27. Not all of the constants for one electronic state were taken from the same journal article, where available, the most recent constants were used in the data. This effects primarily the ground state of  $I^{35}Cl$  because the journal article from which the data was taken (the more recent article) uses the older constants as a part of its data set. The disssociation energy for the B states of both isotopes was calculated using energy values averaged from both molecules. The authors state their doubts about the validity of this number and believe its true value is within five standard deviations rather than one as normally quoted (14:1304).

The Franck-Condon Factors for the three transitions considered follow in Tables 28 through 30. Each set of Franck-Condon Factors exhibits the characteristic Condon Parabola, although the branches of the parabola are fairly far apart. This represents a placement of the states such that the equilibrium internuclear distances are far apart. Literature values of the Franck-Condon Factors are available for only a small portion of one transition, the B to X transition of the (127,35) isotope. The comparison of literature and calculated values is shown in Table 31. As before, the entries in order of occurance are, the literature

TABLE 27

## Data for Iodine Chloride

STATE	(127,35) A (8)	(127,35) B (14)	(127,35) X (8)	(127,37) B (14)	(127,37) X (14)
$T_e$	13742.9	17375.58	0	17375.47	0
$\omega_e$	211.0	204.271	(14) 384.323	200.169	376.093
$\omega_e x_e$	2.12	2.4932	(14) 1.5172	2.5762	1.4522
$B_e$	0.08529	0.086523	0.114157	0.082809	0.109337
$\alpha_e$	7.4 E-4	1.402E-3	5.32 E-4	1.077E-3	5.369E-4
$R_e$	2.685	2.6659	2.32091	2.6667	---
Dis. En.	3814.7	1064.34	17557.6	1064.34	17557.511

All values in inverse cm except  $R_e$  which is in Angstroms

Numbers in parentheses represent bibliographic entry of source article for the number

TABLE 28

Franck-Condon Factors for ICl (35) A to X Transitions

$v''$ $v'$	0	1	2	3	4	5	6	7	8	9	10	11
0	000	000	000	000	001	003	008	020	040	066	092	113
1	000	000	000	001	005	014	033	060	085	093	076	043
2	000	000	001	005	016	036	062	080	071	036	005	003
3	000	001	004	013	033	057	071	056	019	000	019	047
4	000	002	009	026	050	065	051	015	001	025	047	031
5	000	004	016	040	060	052	019	000	023	043	023	000
6	001	007	027	052	056	028	001	015	039	022	000	018
7	002	013	038	056	040	006	006	033	027	001	015	033
8	003	020	047	052	020	000	022	032	005	008	031	015
9	005	028	053	040	005	008	032	016	001	025	020	000
10	008	036	053	024	000	021	027	002	013	026	003	011
11	012	045	048	010	005	029	013	002	024	011	003	024
12	018	052	038	001	016	027	002	013	021	000	016	018
13	024	055	025	001	025	017	001	022	009	004	022	004
14	032	055	013	007	028	005	008	021	001	015	013	001
15	040	050	004	016	023	000	018	012	003	019	002	010
16	049	042	000	024	014	003	021	002	011	013	001	017
17	057	031	002	028	005	010	017	000	017	004	008	014
18	064	020	009	025	000	018	008	005	015	000	015	005
19	069	010	017	018	002	020	001	013	008	004	014	000
20	074	003	024	010	008	016	000	016	001	011	007	004
21	076	000	029	003	015	009	005	014	000	014	001	010
22	075	002	028	000	019	002	011	007	005	011	001	013
23	072	008	023	002	018	000	015	001	011	004	006	009
24	066	018	015	008	013	002	014	000	013	000	011	003

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 28 (cont.)

Franck-Condon Factors for ICl (35) A to X Transitions

$v''$	12	13	14	15	16	17	18	19	20	21	22	23
$v'$												
0	126	128	118	099	049	030	017	009	004	002	001	000
1	013	000	012	043	100	102	087	064	042	025	013	006
2	028	056	060	038	001	021	056	084	094	084	064	042
3	048	022	001	011	056	040	011	000	020	055	082	089
4	004	006	033	044	001	012	042	052	031	005	003	030
5	015	038	028	003	035	038	013	000	022	048	043	016
6	036	017	000	019	017	000	018	039	026	002	008	037
7	013	001	023	030	005	029	028	004	006	033	034	009
8	000	022	026	003	030	016	000	019	032	011	001	024
9	017	025	003	008	011	001	023	023	002	010	031	018
10	026	006	006	025	002	023	017	000	017	026	005	005
11	011	002	022	013	021	016	000	018	021	001	011	027
12	000	016	017	000	017	000	016	018	000	013	022	003
13	008	020	002	010	001	012	018	001	012	020	001	010
14	018	008	003	019	007	019	002	009	019	002	010	020
15	016	000	015	011	018	006	005	018	003	007	019	002
16	005	006	016	000	012	001	016	006	004	018	004	006
17	000	015	006	004	001	011	011	000	015	007	003	017
18	006	014	000	013	004	015	001	010	011	000	015	006
19	013	005	005	013	013	006	004	014	001	010	010	001
20	013	000	012	005	012	000	012	005	004	013	000	010
21	006	003	012	000	004	005	011	000	012	004	005	012
22	000	010	005	004	000	012	003	006	010	000	012	003
23	001	011	000	010	005	010	000	011	002	007	008	001
24	007	007	002	010	010	003	006	008	001	011	001	008

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 29

Franck-Condon Factors for IC1 (35) B to X Transitions

$v''$	0	1	2	3	4	5	6	7	8	9	10	11
$v'$												
0	000	000	000	000	002	006	015	033	061	091	114	127
1	000	000	000	002	007	019	043	071	091	085	055	020
2	000	000	001	005	015	037	062	075	057	020	000	013
3	000	000	002	009	025	049	063	047	013	001	025	050
4	000	000	003	013	033	053	048	017	000	023	045	031
5	000	001	004	017	038	048	028	002	012	039	029	003
6	000	001	006	020	038	038	012	002	028	034	007	004
7	000	001	007	021	036	027	003	009	033	018	000	021
8	000	001	007	021	032	018	000	017	029	005	008	029
9	000	001	007	020	026	011	001	022	020	000	018	024
10	000	001	007	019	022	006	003	023	012	002	024	014
11	000	001	007	017	017	003	006	021	006	006	024	005
12	000	001	007	016	014	001	008	018	002	011	020	001
13	000	001	007	014	011	000	009	015	000	014	014	000
14	000	001	006	012	008	000	009	012	000	015	009	002
15	000	001	006	011	007	000	009	009	001	015	005	005

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 29 (cont.)

## Franck-Condon Factors for ICl (35) B to X Transitions

$v''$	12	13	14	15	16	17	18	19	20	21	22	23
$v'$												
0	128	118	100	077	034	020	011	006	003	001	000	000
1	001	006	032	067	104	096	077	054	035	021	011	006
2	044	062	053	025	005	031	065	088	093	083	064	044
3	044	015	000	016	056	038	010	000	017	049	077	089
4	004	005	032	045	002	008	036	053	041	014	000	012
5	008	034	035	009	026	042	027	003	006	033	050	039
6	029	030	006	005	033	009	002	025	040	024	002	007
7	030	008	003	027	004	006	030	029	006	003	027	038
8	014	000	019	027	005	028	022	001	009	031	024	002
9	002	009	026	010	023	022	001	010	028	016	000	015
10	001	020	018	000	024	004	006	025	014	000	016	028
11	006	023	007	004	011	001	020	018	000	013	024	007
12	014	018	000	012	001	010	021	003	007	022	009	001
13	018	011	001	018	001	018	011	001	018	014	000	014
14	019	005	006	018	007	018	002	008	019	003	006	020
15	017	001	011	014	013	011	000	015	011	000	016	012

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 30

Franck-Condon Factors for ICl (37) B to X Transitions

$\begin{smallmatrix} v'' \\ v' \end{smallmatrix}$	0	1	2	3	4	5	6	7
0	000	000	000	000	002	006	014	031
1	000	000	001	003	009	023	048	077
2	000	000	002	007	021	044	069	077
3	000	001	004	015	035	057	063	040
4	000	002	008	025	047	057	039	008
5	000	003	015	037	054	044	013	001
6	001	006	023	048	053	025	000	015

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 30 (cont.)

Franck-Condon Factors for ICl (37) B to X Transitions

$\frac{v''}{v'}$	8	9	10	11	12	13	14	15
0	056	085	110	126	129	122	104	081
1	096	088	057	021	001	006	033	068
2	054	017	000	018	048	062	047	018
3	007	004	033	053	037	008	002	025
4	003	032	047	022	000	014	040	039
5	025	040	018	000	021	040	022	001
6	036	019	000	019	036	015	000	021

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 31

Franck-Condon Factors for ICl, B to X Transitions  
Comparison of Literature and Calculated Values  
(FCF x 1000)

v''	0	1	2	3	4	5	6	7	8	9	10	11
v'	0	0	0	1	2	7	18	37	63	92	117	131
0	0	0	0	0	2	6	16	36	65	96	120	131
	0	0	0	1	0	1	2	1	2	4	3	0
	0	0	1	3	10	25	48	73	86	77	49	17
1	0	0	0	2	6	19	41	69	88	81	52	18
	0	0	1	1	4	6	7	4	2	4	3	1
	0	0	2	8	22	44	64	67	45	14	0	15
2	0	0	1	4	15	35	61	74	56	20	0	13
	0	0	1	4	7	9	3	7	11	6	0	2
	0	1	4	14	32	50	54	34	7	2	22	42
3	0	0	2	8	24	48	64	49	14	1	24	49
	0	1	2	6	8	2	10	15	7	1	2	7

Order of entries: literature Franck-Condon Factor (5)  
calculated Franck-Condon Factor (14)  
absolute difference of the two values

value of the Franck-Condon Factor, the calculated value, and the absolute difference between the two. The Condon Parabolas outlined in Table 31 show excellent agreement between the two sets of factors. Even the agreement between the values of the Franck-Condon Factors themselves is very good. The comparison is only for low vibrational levels which can account for part of the good agreement. The closeness of the values is even more significant when it is considered that the two sets of factors were calculated from different sets of molecular constants. The literature values are from a 1976 article by Clyne and McDermid (5) using constants obtained from their own spectroscopic observation and search of the open literature while the calculated values used molecular constants from a 1982 article by Hansen and others (14). The conclusion drawn from this is that the B to X transition of the (127,35) isotope of ICl is well known for the lower vibrational levels and that further refinement of molecular constants for these two states will yield improvement primarily in the higher vibrational levels. The combination of more recent molecular constants plus the IPA routine used the calculation of the potentials for this thesis should lead to values of Franck-Condon Factors which are very good at the lower levels and very reliable at the higher vibrational levels.

#### Iodine Monofluoride

Franck-Condon Factors for transitions between two

electronic states of IF were calculated from values for the molecular constants found in the literature. The wavefunctions for the B and X states were calculated from molecular constants found in an article by Clyne and McDermid (5). The molecular constants found in the article are a compilation of values from other journal articles. The molecular constants are listed in Table 32 and the Franck-Condon Factors for the B to X transitions are tabulated in Table 33. The values of the wavefunctions were evaluated at 301 points between the minimum and maximum internuclear distances. Literature values of Franck-Condon Factors are included in the article by Clyne and McDermid. These literature values were calculated using wavefunction values based on purely RKR potentials. A side by side comparison of the literature and calculated values reveals good agreement between the Franck-Condon Factors themselves and very good agreement between the two Condon Parabolas.

#### Discussion of Results

The Franck-Condon Factors for lead oxide were improved by the use of more accurate molecular constants. Because the previous set of factors was calculated using values of the wavefunctions based on potentials approximated by the RKR-IPA program, the old versus new comparison was very close. The most prominent changes were in the higher vibrational levels where changes were expected due to the improved constants. For these comparisons, it can be assumed that any changes in

TABLE 32  
Data for Iodine Monofluoride

STATE	B (5)	X (5)
$T_e$	19054	0
$\omega_e$	406.51	610.51
$\omega_e X_e$	1.30	3.10
$B_e$	0.2272	0.2799
$\alpha_e$	0.001398	0.001887
$R_e$	2.1189	1.9089
Dissociation Energy	11544	22998

All values in inverse cm except  $R_e$  which is in Angstroms  
Numbers in parentheses represent bibliographic entry of  
source article for the number

TABLE 33

Franck-Condon Factors for IF Large B to X Transitions

$v''$	0	1	2	3	4	5	6	7	8	9	10	11
$v'$												
0	005	031	088	157	202	198	153	094	046	018	006	002
1	023	093	151	118	031	002	063	140	158	118	064	027
2	056	138	097	007	031	097	067	004	029	111	147	115
3	096	125	015	030	086	025	010	078	066	004	029	109
4	128	069	006	080	025	015	072	022	012	077	053	000
5	142	017	050	051	005	065	016	021	065	009	026	078
6	138	000	076	005	049	030	013	058	003	039	050	000
7	119	016	059	009	056	000	054	008	032	039	002	057
8	094	045	024	042	020	030	030	014	044	001	050	012
9	070	070	002	058	000	051	000	047	003	039	016	020
10	049	082	004	044	017	029	020	027	016	032	008	042
11	032	080	024	017	043	003	043	000	042	000	040	003
12	020	069	046	001	047	006	032	015	022	019	020	017
13	012	055	061	004	030	028	007	037	000	038	000	037
14	007	040	065	019	009	042	001	032	013	018	022	011
15	004	027	061	038	000	036	018	009	033	000	034	002
16	002	018	050	051	005	018	035	000	030	012	014	024
17	001	011	039	055	019	004	036	011	011	030	000	030
18	001	007	028	052	034	000	024	028	000	028	011	011
19	000	004	019	045	044	008	009	034	007	012	028	000
20	000	002	013	036	048	020	001	027	022	000	026	011
21	000	001	008	027	045	032	002	014	031	005	012	026
22	000	001	005	019	039	039	011	003	028	018	001	025
23	000	000	003	013	032	042	021	000	017	027	003	012
24	000	000	002	009	024	039	030	005	006	027	014	001

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

TABLE 33 (cont.)

## Franck-Condon Factors for IF Large B to X Transitions

v'' v'	12	13	14	15	16	17	18	19	20	21	22	23
0	000	000	000	000	000	000	000	000	000	000	000	000
1	009	002	001	000	000	000	000	000	000	000	000	000
2	064	026	008	002	000	000	000	000	000	000	000	000
3	139	105	054	021	001	000	000	000	000	000	000	000
4	044	120	132	087	013	003	001	000	000	000	000	000
5	030	003	072	133	065	024	006	001	000	000	000	000
6	050	067	008	025	135	092	041	012	003	000	000	000
7	024	010	070	039	067	134	117	061	021	005	001	000
8	023	053	002	041	008	028	115	134	083	032	008	001
9	042	000	050	025	069	033	004	084	140	106	046	013
10	000	045	012	023	000	049	058	001	050	134	125	063
11	036	014	021	036	052	014	021	070	015	022	118	140
12	025	010	036	001	004	034	037	003	064	036	005	094
13	000	038	000	038	031	023	012	051	001	045	056	000
14	026	010	025	014	024	010	040	000	049	014	024	067
15	030	005	029	005	003	037	000	042	005	034	032	007
16	005	030	001	032	033	002	034	006	030	020	016	045
17	005	022	012	016	013	020	015	019	021	013	034	003
18	025	001	029	000	003	027	005	028	004	033	002	041
19	026	008	014	019	026	001	030	000	032	000	035	001
20	008	025	000	026	015	013	012	019	008	024	007	026
21	000	022	011	008	000	027	001	024	006	020	011	019
22	011	006	025	001	010	009	021	002	026	000	028	001
23	024	000	019	014	024	001	021	009	011	019	004	025
24	023	011	004	024	015	016	002	024	001	021	007	014

Values in the table are (FCF x 1000)

Values calculated using Simpson's Rule Approximation

the Franck-Condon Factors occurred because of the new constants and not because of a difference in the modelling of the potential. The same however, can not be said of the calculations done for the interhalogens. Generally, the potentials in the literature were modelled using a straight RKR approximation, without the added accuracy of the IPA routine. When the literature and calculated values of the turning points for the potential are compared, the changes induced by the IPA become apparent. The width ( $R(\max) - R(\min)$ ) of the two energy levels are approximately the same for any vibrational level (the agreement is better at the lower  $V$  levels) but the values of the turning points are shifted towards smaller internuclear distance, as can be seen in Figure III. This shift is not constant for all energy levels however, as might be expected if one of the rotational constants were wrong, but instead gets larger with larger values of  $V$ . This shifting of the RKR-IPA potential from straight RKR values for potentials calculated with the same molecular constants shows the IPA routine at work. Because the iterative processes of the IPA serve to improve the accuracy of the potential (especially at higher vibrational levels) by repeated comparisons and corrections of the potential energy values, these shifted potentials are more accurate than those reported in the literature. Thus, the wavefunctions calculated from improved potentials are more accurate and from them the Franck-Condon Factors gain accuracy. Also, more accurate potentials allow the number of

## TURNING POINT PAIRS

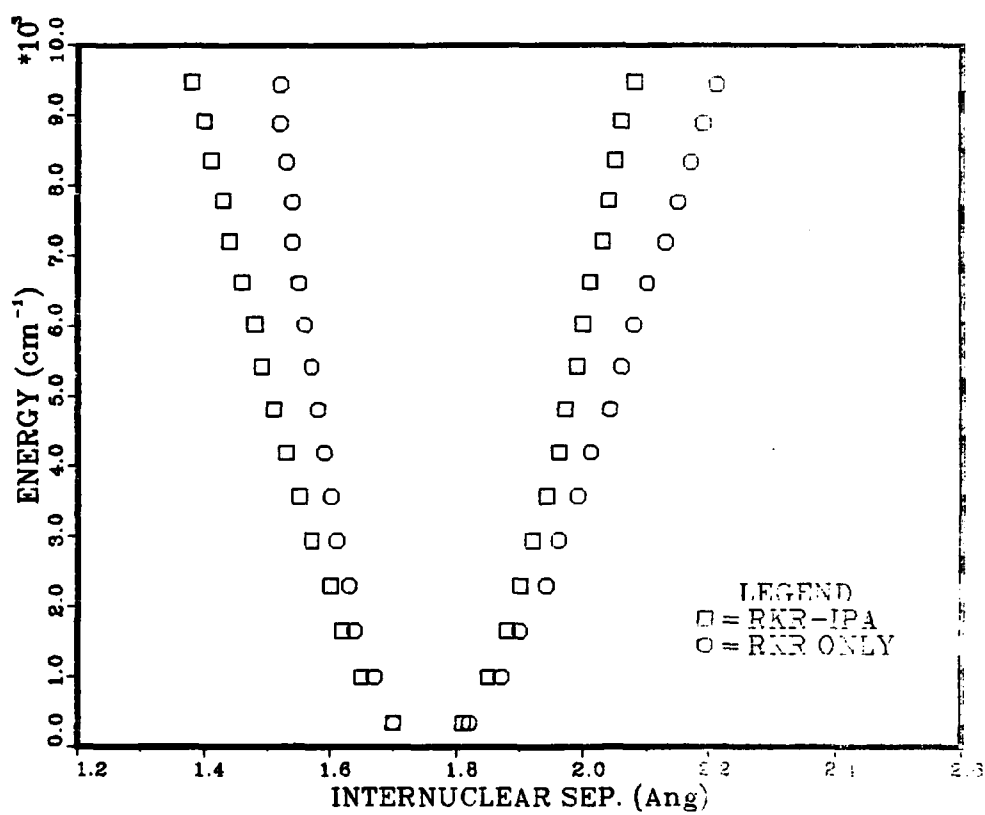


FIGURE III. Comparison of Turning Points for RKR and RKR-IPA Methods. Turning Points shown are for BrF ground state.

vibrational levels and wavefunction values calculated for them to be reliably extended closer to the dissociation energy, providing a more complete knowledge of transition probabilities in a molecule.

## V. Summary and Recommendations

This thesis covers the modelling of potential energy wells using a Rydberg-Klein-Rees approximation plus an optional Inverted Perturbation Approach routine to increase the accuracy of the potential energy curve at higher energies. The wavefunction is approximated for each rotationless vibrational level by calculating its value at a specified number of points along the region of interest. Finally using these tabulated wavefunction values, the Franck-Condon Factors (which are proportional to the transition probability) are calculated for 24 transitions split between a total of six molecules (lead oxide plus five interhalogens). The interhalogens are of special interest to the people at the Air Force Weapons Lab at Kirtland AFB.

This thesis opens with a discussion of the RKR approximation, including when the approximation is used and the Dunham Equation. This equation is not only the starting point for calculation of the potential, but also the equation which defines the molecular constants. The discussion continues emphasizing the importance of the "f" and "g" variables in the calculation of the turning points. The potential is modelled by a set of these turning points (maximum and minimum internuclear separation of the two nuclei) listed in order of increasing energy. This ends the first cut calculation of the potential. The articles reviewed which published the molecular constants, stopped

their work here and calculated the Franck-Condon Factors based on an RKR potential. The recently developed IPA routine was used in this thesis to increase accuracy beyond the RKR analysis. The deviation from a straight RKR approach was most often seen in the higher vibrational levels as a slight shift of the potential curve turning points. The IPA is referred to as an inverted approach because the  $\Delta E_{vj}$  in equation 14 is known and  $\Delta U_0(r)$  is desired, generally the opposite is true. The theory and the procedures of the IPA follow the discussion of the RKR method.

Next, the Franck-Condon Principle and the calculation of Franck-Condon Factors is studied. The principle is described both classically and quantum mechanically and differences between the two are mentioned. Also the concept of transition probability based on the maxima and minima of the wavefunctions of the two states is discussed. The formula for the Franck-Condon Factors is derived from the quantum mechanical statement of the transition moment for two electronic states of a diatomic molecule. Once the final form of the Franck-Condon Factor formula is obtained the factor's relationship to the probability of a transition occurring is more easily seen. The section which calculates the Franck-Condon Factors was upgraded from a simple histogram approach to a Simpson's Rule approximation. The results of this modification were verified by comparing the newly calculated Franck-Condon Factors with a past set calculated using the same input data and the older version of

the program.

Finally, the Franck-Condon Factors themselves were calculated. Nine states were modelled for lead oxide and factors for 10 transitions were calculated. For molecular bromine a total of seven states were modelled using three isotopic forms of the molecule. The Franck-Condon Factors for six transitions (between states of the same isotopic make-up) were tabulated. For bromine chloride, two states each for two isotopes were approximated and the factors for one transition per molecule were calculated. Bromine monofluoride had just two states modelled and one set of Franck-Condon Factors calculated. A total of five electronic states were approximated for iodine chloride split between two isotopic forms. Within these five sets of potential wells three transitions had the factors calculated for them. Finally, two states and one transition were calculated for iodine monofluoride. With the exception of bromine chloride, good agreement between the most probable transitions (the Condon Parabola) for each set of factors was found even though the numerical values of the two sets differed. This shows that the less accurate RKR approach is sufficient for many uses of Franck-Condon Factors.

#### Recommendations

1. The rescaling and shifting subroutines of program FCFACT need to be modified and thoroughly tested. It was discovered late in the quarter that these routines under

special circumstances do not function as expected. The problems are more than likely minor, but the present form of the program forces the two input wavefunctions to be scaled identically and defined on the same range. If this is not done, the program will calculate a set of Franck-Condon Factors which are strongly shifted towards the lower vibrational quantum numbers. Allowing the two sets of wavefunction values to be entered with different scaling factors will increase the power of the program by allowing the most accurate set of wavefunction values for a particular state to be used.

2. The RKR-IPA program should be modified to accept data for a potential which has been calculated by other means. The potential data could be entered as turning points and energy values for each vibrational level and could be drawn from journal articles. The RKR portion of the program would be skipped and the IPA applied to the already existing potential. Several problems of working with literature data could be avoided this way. Examples of these would be cases where the authors used more molecular constants than were reported in the article or if the constants reported contained an extra perturbation term which can not be duplicated. This problem occurred for one molecule (BrCl) in this thesis.

3. Matrix solutions to the Franck-Condon Factor integral should be investigated. Solutions using matrix techniques have been proposed in the literature (12, 1, 25).

These methods would increase the efficiency of the calculation and be a good match to programs currently being developed which model the potential wells using matrix techniques. These techniques become especially important as computer usage and demands for computer time increase.

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## Appendix A

### FCFACT, Revised Code

This appendix contains the upgraded calculation of the Franck-Condon Factors with the Simpson's Rule approximation to the overlap integral. Changes to the program included the addition of the file WFXN which holds the product of the two wavefunction files. Other changes increased the limits over which the integral was evaluated to include the entire interval on which the potential was modelled. The final change made to the program was the upgrade from a simple Histogram approach to a Simpson's Rule Approximation to the overlap integral. None of the Scale, Shift, or Normalization routines were changed. Only the portion of the program which calculates the Franck-Condon Factors is included in this appendix, the other portions of the program remain as listed in Capt Pow's thesis (20).

C		000870
C	BEGIN CALCULATION OF FCF'S. CONSIDER ALL V LEVEL COMBINATIONS.	000877
C	FIRST MULTIPLY WAVEFUNCTIONS TOGETHER FOR TRANSITION OF INTEREST,	000884
C	THEN INTEGRATE BY SIMPSON'S RULE OVER ENTIRE ARRAY. FINALLY	000891
C	CALCULATE THE FCF (SQUARE OF THE INTEGRAL).	000898
C		000905
	IF (NPTLO .LT. NPTUP) THEN	000912
	NPT=NPTLO	000919
	ELSE	000926
	NPT=NPTUP	000933
	ENDIF	000940
C		000947
	DO 20, I=0,NVUP	000954
	DO 25, J=0,NVLOW	000961
	DO 30, K=1,NPT	000968
30	WFXN(K)=WFXNLO(J,K)*WFXNUP(I,K)	000975
C		000982
C	++++ BEGIN INTEGRATION - 'SUM' HOLDS VALUE OF INTEGRAL +++++	000989
C		000996
	SUM=(WFXN(1) - WFXN(NPT))/2.	001003
	DO 40, K=2,(NPT-1),2	001010
40	SUM=SUM + 2.*WFXN(K) + WFXN(K+1)	001020
C		001030
	SUM=2.*SUM/3.	001040
C		001060
C	++++ CALCULATE FCF (SQUARE OF THE INTEGRAL) +++++	001070
C		001080
25	FACTOR(I,J)=SUM*SUM	001090
20	CONTINUE	001100

## Appendix B

### Processing a Batch Job

Programs are run in batch mode either because of the large amount of output generated or because the program requires large amounts of computer memory be available to run. The time required to run a batch job on the Cyber has been greatly reduced with the addition of one system (System B) entirely dedicated to processing batch jobs. If the jobs are submitted during non-peak hours such as weekends or early morning the entire job can be processed by the computer in under two minutes. A run during peak hours may take as long as six hours to be processed.

Batch jobs are submitted using a submit command and a jobfile, which is a file containing the identification of the user and the list of commands to be processed by the computer. The exact form of the jobfile will vary from run to run and from program to program. Two examples are shown in Figures B-1 and B-2. Figure B-1 shows the jobfile for the RKR-IPA program which must have the input data file read external to the main program. Figure B-2 shows the jobfile for program FCFACT. This program contains internal calls for the data files and thus they do not need to be read in by the jobfile. The first four lines of the jobfile are the same for all jobfiles but the rest of the file can have several variations, many of which will accomplish identical tasks.

The specific commands required and their function are covered in the user's manuals written for the Cyber and its operating system. Once the jobfile has been created and saved, the job is submitted using the SUBMIT command, the filename of the jobfile, and a destination for the output (to route output to AFIT, use RB=AF). All of the options for this command are covered in the user's manual for the Cyber.

```
/JOB  
LDB,STCSB.  
USER,T841277,PASSWD.  
CHARGE,*.  
FTN5,L=0.  
LGO.  
SAVE,WAVE.  
/NOSEQ  
/EOR  
/READ,IPA  
/EOR  
/READ,BRFLGB  
/EOF
```

FIG B-1. Jobfile for RKR-IPA

```
/JOB  
LDB,STCSB.  
USER,T841277,PASSWD.  
CHARGE,*.  
GET,BRFBW.  
GET,BRF79XW.  
FTN5,L=0.  
LGO.  
/NOSEQ  
/EOR  
/READ,FCFSMPR  
/EOR
```

FIG B-2. Jobfile for FCFACT

## Appendix C

### Extrapolation of Dissociation Energy from Known Data

In several cases the dissociation energy was not available in the literature in any form, either chemical or spectroscopic. In cases where the other molecular constants were available for more than one molecular form of the same electronic state of the molecule, the values could be extrapolated. The approximation assumes similiarity between these identical states of different molecular forms. To calculate the desired dissociation energy, the value of (Dissociation Energy +  $\omega_e/2$ ) was assumed to be equal for both forms (See equation below). The equation can be set up and solved for the desired energy quickly and calculates dissociation energies consistant with known values.

$$D_e^{(1)} + \omega_e^{(1)}/2 = D_e^{(2)} + \omega_e^{(2)}/2$$

Vita

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↙ This report calculates Franck-Condon Factors for several diatomic molecules ( $\text{Br}_2^{\text{H}}$ ,  $\text{BrCl}$ ,  $\text{BrF}$ ,  $\text{ICl}$ ,  $\text{IF}$ ,  $\text{PbO}$ ). The potential energy wells for the different electronic states of the molecules were modelled using a Rydberg-Klein-Rees approximation. The results of this approximation were further refined using an Inverted Perturbation Approach. Once the potential energy well was approximated by the turning points of the rotationless energy levels, the Schroedinger Wave Equation was solved to get the wavefunctions. From these wavefunctions the Franck-Condon Factors were calculated. Values of Franck-Condon Factors for selected molecules and states are compared to literature values showing good agreement between values calculated in this report and those reported in the literature. Originator supplied

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